THE OPTICAL
ROTATING POWE
OF
Organic Substances and Its Practical Applications

BY

DOCTOR HANS LANDOLT,
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF BERLIN

ASSISTED BY

DR. O. SCHÖNROCK, DR. P. LINDNER, DR. F. SCHÜTT,
DR. L. BERNDT, and DR. T. POSNER

SECOND EDITION

AUTHORIZED ENGLISH TRANSLATION WITH ADDITIONS
BY
DR. JOHN H. LONG,
PROFESSOR OF CHEMISTRY IN NORTHWESTERN UNIV., CHICAGO

ILLUSTRATED

EASTON, PA.:
THE CHEMICAL PUBLISHING CO.
1902

555

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PREFACE TO THE FIRST EDITION

Although the subject of the optical rotating power of organic substances, in theoretical as well as in practical relations, has been growing in importance for a long time, chemical literature possesses thus far no work which presents a complete discussion of the whole field, and studies in this line may be carried out only by the aid of articles scattered through the journals. I have attempted in the present book to supply the want in this direction, and the incentive to the work was furnished by an article which I published some time since in Liebig's *Annalen der Chemie*, Vol. 189. This article dealt with the determination of the specific rotation of solid substances, and was introduced by a short general discussion of optical activity. From several quarters I was urged to enlarge the article, and, especially by the addition of a description of all the new polarization instruments and the practical uses which may be made of them, to work up a monograph as complete as possible of the subject of optical rotation. Such an undertaking appears all the more inviting since in the last few years different observers have carried out investigations in this field which have increased our knowledge considerably, and which make it possible to give a certain degree of completeness to the treatment of the subject.

From a theoretical standpoint the optical activity of organic substances possesses this great interest, that it is a consequence of a peculiar arrangement of the atoms within the chemical molecule, and therefore stands in close relation to the question of constitution. However, we are just at the beginning of investigations of the relations between rotating power and chemical structure, and for future study there is material at hand abundant and full of promise. To lessen the labor in work of this kind, especially in such cases where results may be obtained only by aid of exact measurements, it became necessary to go fully into the discussion of the methods for the determination of specific rotation. Therefore, the use of the different kinds of polarization instruments called for detailed treatment, and besides this the determination of other experimental data, the specific gravity, for example, should be explained In this work I have taken pains to give methods of the greatest possible exactness and to indicate always the limits of accuracy which may be reached in the numerical results If for any special purpose less rigid care is permissible in work the observer will see for himself how the procedure may be simplified.

In a practical direction, as is well known, optical rotation has long since found an important application in the determination of sugar; and recently the optical analysis of other substances, especially that of the cinchona alkaloids, has been also developed. The methods applied in such cases are fully discussed in the book; for the sugar chemist the description of the various saccharimeters and the corrections which must be applied in using them may be of interest, and in part new

The optical introduction, which possibly may be of interest to many chemists, has been kept as concise and elementary as possible. I have also touched but briefly on the relations between crystalline form and rotating power, as this topic appears to belong in the field of physical crystallography

Finally, the table of contents gives full information concerning the subjects treated. HANS LANDOLT.

AACHEN, January, 1879.

PREFACE TO THE SECOND EDITION

The first edition of this work, which appeared in 1879, presented a general view of our knowledge of optical rotation as it existed at that time. Now, after the lapse of eighteen years, when a new edition corresponding to our present position is called for, we have to deal with a task of entirely different dimensions. The progress which has been made in the last two decades in the field of optical activity rests, so far as the theoretical side is concerned, mainly upon the great interest aroused among chemists by the hypothesis of van't Hoff and LeBel on the relation between rotating power and the atomic structure of carbon compounds. Since 1879, when this doctrine was still in its infancy, numerous investigations suggested by it have been carried out, the results of which have abundantly confirmed the theoretical requirements in all cases, so that today the theory may be presented in complete and fully developed form A marked widening of our knowledge may be observed in other directions also ; for example, with reference to multirotation, the causes of variation in specific rotation, rotation dispersion, etc In a practical direction progress has been made in the improvement of polarization apparatus and in the development of methods of optical analysis In addition, the number of optically active substances known has increased since 1879 from 300 to over 700

From the whole range of material now available I have worked up certain parts only myself, which are in brief, the subjects discussed in the following theoretical portions of the book .

Part I. General Conditions of Optical Activity.
Part II. Physical Laws of Circular Polarization.
Part III Numerical Values for the Rotating Power. Specific Rotation.

In a section of Part I dealing with the decomposition of racemic bodies by fungi I have received valuable assistance from Herrn Prof. Dr. P. Lindner, Department Director of the Institute for Fermentation Industries in Berlin, he has had the kindness to prepare a chapter on the subject of the fungi and the forms suitable for resolution, the methods of pure culture and experiments in resolution. I am no less indebted to Dr. W. Marckwald and Prof. Dr. H. Traube, who have rendered me assistance in many questions of stereochemistry and crystallography.

In order to secure a more rapid completion of the following parts of the book I was obliged to seek the cooperation of others, and to the extent as now to be explained

Part IV "Apparatus and Methods for the Determination of Specific Rotation," by Dr. O. Schönrock, Assistant in the Physikalisch-Technischen Reichsanstalt This section presents, first, a description of the different polariscopes and saccharimeters, which in the last few years, and especially through the work of Lippich, have reached such a degree of perfection that they may now be classed among the most exact of instruments for physical measurements. In order to understand these instruments and the methods of using them, it was necessary to discuss, not only their construction, but also, especially, the optical theory on which their use is based, and it was further necessary to go into an accurate definition of the kinds of light employed in determining angles of rotation, particularly the sodium light. The author has discussed this subject in detail which had never before been handled as a connected whole. This was all the more desirable since there can be no doubt that the marked discrepancies found in the determination of the specific rotation of the same substance by different observers do not always depend on impurities in the material used, but very largely on improper manipulation of the polariscope, or on variations in the character of the sodium light employed. It may be further remarked here that a consideration of these sources of error carries with it no increased difficulty in the methods of observation, as one might, at first thought, assume

The section embraces in addition a discussion of all known methods for determination of rotation dispersion, a subject which up to the present time, has not been covered in its related bearings. Finally, the chapters on sodium lamps and polarization tubes follow, and something on the preparation of solutions and the determination of specific gravity, which, as compared with the corresponding parts of the earlier edition, are greatly enlarged

In the preparation of this whole section the author was in position to make use of the experience gained in many investigations of the Physikalisch-Technischen Reichsanstalt.

Part V. "The Practical Applications of Optical Rotation" was written by Dr. F Schutt, Royal Councilor and Permanent member of the Patent Office. As regards saccharimetry, which makes up the larger part of the section, it may be remarked that it was considered the most satisfactory to follow the methods officially adopted in the German Sugar Tax Law of May 27, 1896, and to present these literally. Among other methods of polarimetric analysis those concerned with the determination of cinchona alkaloids are shortened as compared with what was given in the first edition, while, on the other hand, some new methods have been added.

Part VI. "The Constants of Rotation of Active Bodies" has been compiled mainly by Dr. L Berndt and Dr Th Posner, formerly assistants in the II Chemical Laboratory of the Berlin University. The section on ethereal oils was prepared by Dr Rimbach, and Prof Dr. Thierfelder had the kindness to assist in securing the data on bile acids and proteids A few chapters remained in my hands.

In the preparation of this collection of experimental data it was not found possible to include all the statements given in the literature, as this would have unduly increased the size of this part of the work. It was sufficient in many cases to quote observations in part and refer in a note to the original articles. For the same reason any data on the methods of preparation of the substances observed had to be omitted, although such information might often have been found valuable. The search through the literature, in which, however, the possibility of overlooking certain data could not be wholly excluded, was complete to about the middle of 1896. From that date it was only partial. In arranging the substances in order the most consistent system may not always have been followed, but by aid of the alphabetical index it will be possible to find any body described

It is hoped that the work in this new edition also will fill its place as a text- and handbook in presenting a complete résumé of our knowledge on the subject of optical rotation.

H. LANDOLT.

BERLIN, December, 1897

TRANSLATOR'S PREFACE

The two editions of this work which appeared in Germany in 1879 and 1898 enjoyed there a great and well-deserved popularity. A translation of the first edition was brought out in England in 1882, under the title: "Handbook of the Polariscope and Its Practical Applications," and contributed not a little to the advance of methods of optical analysis in that country and the United States Both the original edition and this translation have been, however, long out of print

The scope of the second edition, a translation of which I have the honor of presenting to American and English readers, is much wider than that of the first; the main points of difference are made plain in the author's preface, but attention may be called to the fact that the detailed discussions in Sections IV and V of Part I on the relations between the rotating power and the chemical constitution of carbon compounds, along with the full numerical data on constants of rotation, etc , render the work of the highest value to investigators in many fields of pure organic chemistry Some of the most important advances in this direction are those which have been made in the methods for the resolution of racemic compounds This subject is thoroughly treated by the author, and permission was also given to include still more recent work in the English edition. The sections which I have added in this connection relate to the resolution of asymmetric nitrogen and sulphur compounds and to several new general processes of resolution

I have made also many additions to the numerical values in Part VI, on Constants of Rotation The data for a few of these were sent me by the author, while the others were taken from the journals of the three years following the publication of the German text.

By an arrangement between the publishers, the cuts for the illustrations of the original work become the property of the

American publisher and are used in the translation This will account for the appearance of some German words in connection with a few of the illustrations

In conclusion I wish to acknowledge my indebtedness to my colleagues, Professors Crew and Dains, of Northwestern University, and to Dr. H. W. Wiley, of Washington, for several suggestions of value, and to my assistant, Mr. Frank Wright, for help in the reading of proof

J. H. LONG

CHICAGO, January, 1902

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PART FIRST

General Conditions of Optical Activity

I. INTRODUCTION, DEFINITIONS, AND FORMULAS OF CALCULATION

1. **Active Bodies.**—Those substances which possess the property of rotating through a certain angle the plane of polarization of a ray of polarized light which passes through them are designated as *optically active*, or *circularly polarizing*, while the property itself is described as *optical rotating power*.

The property of optical activity is shown by . 1. A number of inorganic and organic substances in crystalline condition. 2 By a large number of carbon compounds when exposed to the polarized ray in liquid or dissolved condition. In bodies of the first class the cause of the optical activity is due to peculiarity of crystalline structure, while in the second it is due to an unsymmetrical arrangement of the atoms within the molecule.

According to the direction in which the rotation of the plane of polarization takes place active bodies are either ·

Dextrorotatory, with the sign + or *d*,
Laevorotatory " " -- or *l*

If an organic *d*-compound be subjected to chemical transformation, the derivatives may be in part also right rotating, or they may be in part even left rotating. In order to indicate the derivation from the original parent substance, the letter, *d*, is retained as a prefix for all bodies of the group, without, however, expressing by it the direction of rotation in the derivative. If this, also, is to be shown, it can be done by the addition of the + or — sign. The expressions, *d* (+) and *d* (—), indicate right and left rotating derivatives of a dextro-parent substance, while *l* (--) and *l* (+) indicate the direction of rotation of the derivatives of a laevorotating substance.

Many bodies occur in isomeric forms with optically different behaviors. There are recognized

1. Active modifications, found always in two forms constituting the so-called optical antipodes, inasmuch as under like conditions, one form rotates as strongly to the right as the other to the left These are designated as the *d*-form and the *l*-form.

2. Inactive modifications which are mixtures or compounds of the active antipodes in equal proportions, and which may be split up into these by the action of certain agents. For these so-called *racemic* bodies, the symbols *r* or *dl*, or (*d* + *l*) are in use.

3. Inactive modifications which cannot be decomposed into the active forms These will be indicated by *i*[1] in the following pages.

2. **Measure of Rotating Power, Specific Rotation.**—In active crystals the observed angle of rotation varies with the thickness of the plate used, and it is customary to reduce this rotation to that of a plate 1 millimeter in thickness for comparison

In order to express the optical activity of dissolved solid or of liquid carbon compounds the conception of *specific rotation*, introduced by Biot, is employed By this term is understood *that angle of rotation which a liquid would produce if it contained in one cubic centimeter one gram of active substance, and opposed a column one decimeter in length to the passage of the polarized ray*. This datum calculated from observation is represented, following Biot's suggestion, by the symbol $[\alpha]$.

The following points concerning specific rotation may be noticed here in passing; a fuller discussion being reserved for a later chapter. As experiment has shown the angle of rotation produced in a polarization apparatus by an active liquid is dependent on ·

1. The length of column through which the light passes, and is in fact exactly proportional to this length.

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[1] The letter *i* is often used to indicate racemic compounds, but it appears better to use it only for the inactive bodies which cannot be split up. In order to avoid danger of confusion with iso-compounds which are sometimes indicated with *i*, it would be better to use for these the letter *I*. The use of *r* instead of *d* for right rotating substances should be wholly discarded, inasmuch as it does not conform to international use, and because, further, it is already applied to racemic bodies

2. *The wave length of the light ray employed.*—As in the case of refraction of ordinary light the rotation in general increases with decreasing wave length; it is therefore least for red and greatest for the violet rays. Commonly homogeneous yellow light, corresponding to the Fraunhofer line *D*, is employed in the observations. By measuring the rotation for different rays the *rotation-dispersion* of the substance is determined

3. The temperature of the liquid.—With certain substances this has but little influence, but in many others it produces either an increase or a decrease in the angle of rotation. As a normal temperature, 20° C. should be taken

The following observations are required to determine the *specific rotation* of substances which are in themselves liquids:

α. The amount of rotation to the right or left for a definite color, and expressed in circular degrees, and decimals of the same. (The use of minutes and seconds is not customary.)

l. The length of the observation tube, in decimeters.

t. The temperature of the liquid in the tube.

d. The density of the liquid at the temperature, *t*, and referred to water at 4° C. as the basis, in which case *d* expresses the weight in grams of one cubic centimeter. If the density is found by aid of a pycnometer which holds at the temperature of 20° *W* grams of water, and *F* grams of the liquid, then

$$d_4^{20^\circ} = \left(\frac{F}{W} \times 0.99705\right) - 0.00120.$$

According to the above definition, the specific rotation is expressed by the formula:

$$\text{(I)} \qquad [\alpha] = \frac{\alpha}{l.d.}$$

If the kind of light used and the temperature are also added the specific rotation is a characteristic constant of the substance in question. For example, for nicotine:

$$[\alpha]_D^{20^\circ} = -161.55^\circ.$$

Solid active substances are brought into solution by aid of inactive solvents. The preparation of solutions may be effected in two ways:

1. By the aid of a measuring flask the contents of which, in true cubic centimeters at a definite temperature (as 20°C.), is known. A certain weight of the active substance is weighed into the empty flask, the solvent is added to effect solution, and then filled up to the mark. From this we have:

c. The concentration, that is the number of grams of active substance in 100 cubic centimeters of solution, and the specific rotation follows, under the assumption that the rotation is proportional to the concentration, by:

$$[\alpha] = \frac{100\alpha}{l.c} \tag{II}$$

2. A weighed amount of the active substance is dissolved in the liquid in a flask which may be stoppered, and the weight of the solution determined. From these data there may be calculated

p the per cent amount of active substance.
q the per cent amount of inactive solvent

Then, in order to find the concentration of the solution, its specific gravity, d, at a definite temperature, as 20°, must be found As $pd = c$, then:

$$[\alpha] = \frac{100\alpha}{l\,p\,d} \tag{III}$$

This last method is to be applied when it is desired to investigate the dependence of the specific rotation of a body on the composition of its solution.

In stating the specific rotation of a dissolved substance the solvent must always be given, also the concentration or the percentage strength with the specific gravity. Observations may be expressed in the following form For example

$$\text{Laurel camphor}\begin{cases}(98 \text{ per cent alcohol, by volume, } c = 25.35),\ [\alpha]_D^{20} = +44.90^\circ. \\ (\text{glacial acetic acid, } p = 39.72,\ d_4^{20} = 1.0113),\ [\alpha]_D^{20} = +47.18^\circ.\end{cases}$$

As experience has shown there are certain substances for which the specific rotation, as calculated from solutions of different concentrations, remains constant or at most suffers but a very slight change. For such bodies, for example, cane-sugar or milk-sugar dissolved in water, the angle of rotation is exactly proportional to the concentration, and therefore by the following formula,

$$\text{(IV)} \qquad c = \frac{100\alpha}{l[\alpha]},$$

the strength of a solution of the substance may be found if the value of $[\alpha]$ is known. Polarimetric analysis, especially of sugars, is based on this fact.

With the great majority of active substances, however, it has been observed that the specific rotation increases or decreases, with increasing dilution of the solution, and at very different rates for different substances; sometimes the direction of rotation, even, may change. In such cases, there must be an alteration of the nature of the substance by the action of the solvent If the value of $[\alpha]$, for a number of solutions of different strengths has been found, it will be possible to express the dependence of the specific rotation on the factors p and q by the following formulas, in which the constants, A, B, and C, or a, b, and c are determined by experiment·

$$\text{(V)} \qquad [\alpha] = A + Bq$$

$$\text{(VI)} \qquad [\alpha] = a + bp,$$

or

$$\text{(V}'\text{)} \qquad [\alpha] = A + Bq + Cq^2$$

$$\text{(VI}'\text{)} \qquad [\alpha] = a + bp + cp^2$$

In the formulas, (V) and (V′), the constant A expresses the specific rotation of the active substance in undiluted condition, while B and C show the change produced by 1 per cent. of the inactive solvent. If q is taken equal to 100, the specific rotation in infinite dilution is given.

In the formulas, (VI) and (VI′), the constant a corresponds to the specific rotation in infinitely great dilution, while the value for the pure substance is given when p is taken equal to 100.

If it be desired to replace the constants, A and B, by a and b in the formulas, (V) and (VI), and *vice versa*, we take

$$A = a + 100\,b \qquad\qquad a = A + 100\,B$$
$$B = -\,b \qquad\qquad\qquad b = -\,B$$

In the 3-term formulas, we have:

$$A = a + 100\,b + 10{,}000\,c \qquad a = A + 100\,B + 10{,}000\,C.$$
$$B = -\,b - 200\,c. \qquad\qquad b = -\,B - 200\,C.$$
$$C = c. \qquad\qquad\qquad c = C.$$

If, further, the constants of the equation,

$$[\alpha] = a + bp + cp^2,$$

have been determined for an active substance, with molecular weight *M*, and if it be desired to alter them, so as to make them apply for a derivative (hydroxide or salt, for example), with the molecular weight *M'*, which leads to the formula,

$$[\alpha]' = a' + b'p + c'p^2,$$

then, we place:

$$a' = a\,\frac{M}{M'}\,,\quad b' = b\left(\frac{M}{M'}\right)^2\quad c' = c\left(\frac{M}{M'}\right)^3$$

3. **Molecular Rotation.**—This term is applied to the product of the molecular weight and specific rotation of a body, and is represented by the symbol [*M*]. But, to avoid the use of inconveniently large numbers, it is customary to take the one-hundredth part of this product; thus.

$$[M] = \frac{M}{100}\,[\alpha]$$

In this case, [*M*] expresses the rotation which would follow, if each cubic centimeter of the solution contained 1 gram-molecule of the active substance, and the length of the liquid column were 1 millimeter. The molecular rotation is applied in making stoichiometric comparisons

4. **Historical.**—The rotation of the plane of polarization was noticed first in quartz plates by Arago, in 1811. In 1815 Biot and Seebeck discovered the optical activity of certain organic substances (oil of turpentine, and aqueous solutions of sugar and tartaric acid). Through a long series of investigations, extending over a period of 47 years (from 1813 to 1860),

Biot established the important physical laws and the general nature of the phenomena observed. In 1823, Fresnel published a theory of the effects as noticed in quartz in which he introduced the term *circular polarization*. In 1831, Herschel discovered the important relation existing between the rotating power in quartz crystals, and the development of their faces. A further fundamental discovery in this field was made by Pasteur, who found in 1848, in the examination of tartaric and racemic acids, that one and the same active substance may occur in oppositely rotating and in inactive modifications. The last great advance in the subject was brought about in 1874 by van 't Hoff and LeBel, who independently discovered the relation existing between the rotating power of organic substances and their atomic constitution, in the discussion of which the notion of asymmetric carbon atoms was introduced in the science

II. CLASSIFICATION OF ACTIVE SUBSTANCES

5. Preliminary Remarks, Relation of Crystalline Form to Rotation.—All bodies which in crystalline condition or in solution have the power of rotating the plane of polarization of light crystallize, as was shown by Pasteur,[1] in so called *hemihedral* forms, and the crystals of the right and left modifications of an active substance are *enantiomorphous.*

A hemihedral crystalline polyhedron is not superposable on its mirror image The original form and that corresponding to its image are related as is the right hand to the left; they exhibit the peculiarity described in crystallography as *enantiomorphism.*

Hemihedral forms, from a geometric standpoint, can possess axes of symmetry only, but no center of symmetry and no planes of simple or compound symmetry.[2]

In the thirty-two possible crystalline groups, eleven are found with hemihedral forms, and these are given below with the nomenclature of Liebisch, and also that of Groth in parenthesis

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[1] Pasteur. Compt. rend., **26**, 535, **27**, 401, **35**, 180 Compare also Becke Min. und petrogr Mitth v Tschermak, **10**, 414 (1889), **12**, 256 (1891)

[2] For details on the symmetry relations in enantiomorphous forms consult the works of Th Liebisch. Grundriss der physikalischen Krystallographie, Leipzig, 1896 P Groth · Physikalische Krystallographie, 3 Aufl, Leipzig, 1895.

I. Regular System

1. Plagihedral-hemihedral (pentagon-icositetrahedral) group.
2. Tetartohedral (tetrahedral-pentagondodecahedral) group.

II. Hexagonal System

3. Trapezohedral-hemihedral (hexagonal-trapezohedral) group.
4. First hemimorph-tetartohedral (hexagonal-pyramidal) group.
5. Trapezohedral-tetartohedral (trigonal-trapezohedral) group.
6. Octahedral (trigonal-pyramidal) group

III. Tetragonal System

7. Trapezohedral-hemihedral (trapezohedral) group
8. Hemimorph-tetartohedral (pyramidal) group

IV. Rhombic System

9. Hemihedral (bisphenoidal) group

V. Monoclinic System

10. Hemimorphic (sphenoidal) group

VI. Triclinic System

11. Hemihedral (asymmetric) group.

In all cases in which a complete determination of the crystalline symmetry of the bodies under consideration could be carried out the statement made above, that optical rotation in a crystal is always associated with enantiomorphism, has been confirmed.[1] As experience has shown, this rule is not reversible; that is, if the crystals of a body are found to be hemihedral the conclusion can not be drawn that in either the solid or dissolved form it will show circular polarization. For example, the following compounds crystallize in hemihedral forms, NH_4Cl, $Ba(NO_3)_2$, $Li_2SO_4 + H_2O$, $NiSO_4 + 6H_2O$, $Sr(CHO_2)_2 + 2H_2O$, but they are inactive in solid form as well as in solution.[2]

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[1] Liebisch. Loc cit., p 41 and 426

[2] Objections to Pasteur's law have been raised by Wyrouboff. Ann chim phys. [6], **8**, 416; [7], **1**, 10 Also by Walden Ber. d chem. Ges., **29**, 1692 Traube replied to this *Ibid*, **29**, 2446

Optically active substances may be divided into three essentially distinct classes:

6. *First Class* —**Bodies which possess the property of rotating the plane of polarized light only in the crystallized condition, and which lose this property when brought into the amorphous condition by fusion or solution.**

Circular polarization has been noticed only in crystals belonging to the regular, hexagonal, and tetragonal systems; that is, in groups 1 to 8 of the above scheme. At present the following organic and inorganic bodies are known to belong here:

Regular System.

Group 2	Sodium chlorate	$NaClO_3$.
	Sodium bromate	$NaBrO_3$.
	Sodium sulphantimonate	$Na_3SbS_4 + 9H_2O$.
	Sodium uranyl acetate	$NaUO_2(C_2H_3O_2)_3$.

Hexagonal System.

Group 4	Potassium lithium sulphate	$KLiSO_4$
	Ammonium lithium sulphate	$(NH_4)LiSO_4$.
	Rubidium lithium sulphate	$RbLiSO_4$
	Potassium sulphate lithium chromate	$K_2SO_4 + Li_2CrO_4$
Group 5	Quartz	SiO_2
	Cinnabar	HgS
	Potassium dithionate	$K_2S_2O_6$.
	Rubidium dithionate	$Rb_2S_2O_6$.
	Calcium dithionate	$CaS_2O_6 + 4H_2O$
	Strontium dithionate	$SrS_2O_6 + 4H_2O$
	Lead dithionate	$PbS_2O_6 + 4H_2O$.
	Benzil	$C_6H_5.CO\ CO\ C_6H_5$

(Rubidium and cesium tartrates, laurel camphor, and matico-camphor belong to Class II)

Group 6	Sodium periodate	$NaIO_4 + 3H_2O$.

Tetragonal System.

Group 7	Ethylene diamine sulphate	$(N_2H_4.C_2H_4)H_2SO_4$.
	Guanidine carbonate	$(CH_5N_3)H_2CO_3$
	Diacetyl phenolphthalein	$C_{20}H_{12}(C_2H_3O_2)_2O_4$
	Sulphobenzene trisulphide	$(C_6H_5.SO_2.S)_2S$.
	Sulphotoluene trisulphide	$(C_7H_7.SO_2.S)_2S$.

(Strychnine sulphate belongs in Class II.)

The optically active single-refracting crystals belonging to the regular system show rotation of the plane of polarization equally strong in all directions, as was shown especially by Sohncke,[1] in the case of sodium chlorate. In the cases of hexagonal and tetragonal crystals, which are uniaxially double-refracting, the phenomenon of circular polarization may be observed only in the direction of the optical axis, and plates for this purpose must therefore be cut perpendicularly to this axis. In normal biaxial crystals belonging to the rhombic, monoclinic and triclinic systems the rotating power has not yet been observed, and as Wiener[2] has shown, it cannot be found in all those cases where there is at the same time strong double refraction.

All the active crystals which have been mentioned above

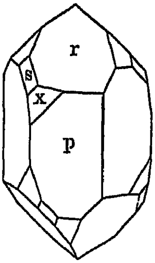

Fig 1

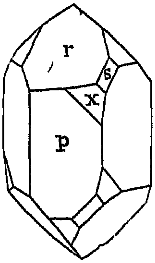

Fig 2

occur in right- and left-rotating varieties, which exhibit equal activities for equal thicknesses of layers passed by the light The direction of rotation stands in relation to the condition of enantiomorphism in the crystal, which is often shown in the geometric development of the latter by the appearance of so-called hemihedral or tetartohedral surfaces, oppositely located in different individual crystals. The best known illustration of this is found in hexagonal, trapezohedral-tetartohedral quartz, in which the tetartohedral surfaces, *s* and *x*, very often appear, and in such a manner that in right-rotating crystals (Fig. 2), the surface, *s*, lies to the right of *x*, while in left-rotating crystals (Fig. 1), it lies to the left of *x*. The one

[1] Sohncke Wied Ann., 3, 530

[2] Wiener. Wied. Ann, 35, 1

form is the mirror image of the other. Analogous relations are found in other crystals of the class.[1]

The extent of rotating power, for equal thicknesses of layer passed by the light, is very different in different active crystals. The following table gives the data thus far found for plates of 1 millimeter thickness, and for light of different wave lengths. The latter, expressed in millionths of a millimeter ($\mu\mu$), correspond either to the Fraunhofer lines, *C*, *D*, *E*, *F*, *G*, to mean yellow light, *j*, or to the lines from lithium, sodium, and thallium. The bodies are arranged in the order of their rotating power for the line *D*.[2]

Crystalline mixtures of isomorphous active crystals exhibit a rotation which is nearly proportional to the percentage composition and amount of rotation of the components. The proof of this rule has been given mainly by Bodländer[3] from investigations of various crystallizations of lead dithionate and strontium dithionate.

Behavior of active crystals in powdered condition.—The question as to whether the rotating power of fine particles is the same as that of the larger crystal, or whether it decreases when the particles have reached a certain degree of fineness has been tested by Landolt[4] with sodium chlorate.

In crystalline plates 1 millimeter in thickness the salt shows a rotation for white light, $\alpha_j = \pm 3.54°$, and as its specific gravity is $d = 2.488$ the specific rotation must be $[\alpha]_j = a/d = \pm 1.42°$. If the crystals are rubbed as fine as possible and the powder so obtained be suspended in a mixture of absolute alcohol and carbon disulphide, the composition of which may be varied until a clear liquid is obtained, that is, until the mixture has the same refractive index as the salt particles, then it is found on examination in a polarization tube

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[1] All these cases are discussed in the works of Groth and Liebisch, already referred to.

[2] Besides these the following observations have been made which refer to green light not specially defined:

Strontium dithionate......................1.64°
Calcium dithionate...................... 2.09°
Pape. Pogg. Ann., **139**, 224, (1870).

Full data are given for quartz and sodium chlorate in the chapter on "Rotation Dispersion."

[3] Bodländer. Inaug. Diss. Breslau, 1882; Wied. Beib., 7, 396.

[4] Landolt: Sitzungsber. der Berl. Akad., 1896, 785; Ber. d. chem. Ges., **29**, 2404.

(1 to 1.5 decimeter in length) that the suspended substance shows the right or left rotation of the original crystals. In order to keep the powder evenly distributed through the liquid it is necessary to rotate the polarization tube on its axis In such experiments in which the diameters of the particles were mostly between 0.004 mm and 0.012 mm. or even between 0.003 and 0.007 mm. the specific rotation[1] was found as $[\alpha]_j = \pm 1.36°$ to 1.49°, or, in the mean, ± 1 41°, referred to a layer 1 mm. in thickness As this value agrees exactly with that found for the large crystals it follows that in powdering to the degree mentioned the active crystalline structure has not suffered the slightest change The question, what size the smallest particle which still shows circular polarization must have, and of how many single molecules it must be composed, remains unanswered.

The optical activity of sodium chlorate disappears completely in aqueous solution, and even when this is in supersaturated condition. If the salt be precipitated by addition of alcohol, the crystalline precipitates formed, and from solutions of either right or left rotating crystals, are found to be, when examined in the suspended condition, either inactive or to show one of the two directions of rotation. The specific rotation is, however, always smaller than the normal (± 1 41°), from which it follows that the precipitates are mixtures of right and left salts. Which of these predominates depends on the direction of rotation of the particles which first separate Bearing on this it may be said that when one of two portions of a saturated solution is treated with a trace of the solid right-rotating salt, and the other with a trace of the left-rotating salt and then precipitated by alcohol, the precipitates formed are found to rotate accordingly.

On the cause of rotation in crystals see §§ 9 and 10.

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[1] The specific rotation of solid active particles is expressed, as in the case of solutions by $[\alpha] = av/lp$, when a is the angle of rotation, l the length of tube, v the volume of the same and p the weight of the powder suspended

Color	Red		Yellow		Green		Blue	Indigo	
Wave length in $\mu\mu$	670 8	656 2	589 2	556	535 1	526 9	486 1	430 7	Observer[1]
Line	*Li*	*C*	*D*	*j*	*Tl*	*E*	*F*	*G*	
Uranylsodium acetate	....	....	1 48 *a*	1 8 *b*	. .	...	..	...	1 *a*, 1 *b*
Potassium sulphate-lithium chromate	.	....	1 93	.	..	....	....	....	2
Sodium sulphantimonate	....	....	....	2.67	....	...	...	..	3
Sodium bromate	...	....	2 17 *a*	2 8 *b*	...	....	....	....	4 *a*, 4 *b*
Sodium chlorate	....	2 51	3.14	3.54 *a*	....	3 95	4.64	5 95	5, 5*a*
Potassium lithium sulphate	....	....	3.44	.. .	....	...	.. .	...	6
Lead dithionate	....	4 09 *a*	5 53 *a*	6.34 *b*	...	7 25 *a*	8 88 *a*	...	7 *a*, 7 *b*
Potassium dithionate	....	6 18	8.39	....	.	10 51	12 33	....	8
Guanidine carbonate	12 58	...	14 58	....	17 07	. .	....	....	9
Ethylene diamine sulphate	....	.. .	15 50	..	....	. ..	...	. ..	10
Diacetylphenolphthalein	17 10	.. .	19 70	....	23 80	....	.	....	11
Quartz	16 43 *b*	17.31 *a*	21.718*c*	24 5 *d*	26 66 *b*	27 54 *a*	32 76 *a*	42.59 *a*	12 *a*, *b*, *c*, *d*
Sodium periodate	....	19 40	23.3	....	. .	28 5	34 2	47 1	13
Benzil	....	. ..	24.84	. ..	. .	....	. ..	. ..	14
Cinnabar	270—300		....	..	....	....	....	...	15

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[1] Observers 1 *a*—Hermann Traube Landolt-Boernstein s Phys chem Tab, 2 Ed 459 1 *b*—Marbach Pogg Ann 94, 412 (1855). 2—H Traube *l c* 3—Marbach Pogg Ann, 99, 451 (1856). 4*a*.—H. Truabe *l c* 4b—Marbach Pogg Ann, 94, 420 (1855). 99, 457 5—Mean of the determinations of Sohncke [Wied Ann 3, 529,] and Ch E Guye [Arch d Gen. (3) 22, 130 (1889], See the chapter on Rotation-dispersion. 5a—Marbach Pogg Ann, 91, 482 (1854), 94, 419, 99, 451 6.—H Traube N Jahrb f Mineral, 1894, I, 178 7 *a*—Pape Pogg Ann, 139, 224 (1870) 7 *b*—Bodlander Groth's Ztschr f Kryst 9, 309 (1884) 8—Pape Pogg Ann, 139, 224 (1870) 9—Bodewig · Pogg Ann, 157, 122 (1876) 10—v Lang Wien Ber, 65, (2) 30 (1872) 11—Bodewig Groth s Zeitschrift, I, 72 (1877) 12 *a*—Soret and Sarasin C r, 95, 635 (1882) See the chapter on Rotation-dispersion 12 *b*—v Lang Wien. Ber, 74, (2) 209 (1876) 12 *c*—Gumlich, Wiss Abhand d phys-tech Reichsanstalt, 2, 201 (1895) 12 *d*—Biot Broch 13—Groth Pogg Ann, 137, 433 (1869) 14—Des Cloizeaux C r 68, 308 (1869), 70, 1209 (1870). 15—*Ibid*, 44, 876, 909 (1857)

7. *Second Class.*—**Bodies which rotate in both crystalline and amorphous form, in solution or in fused condition.**

But six compounds of this class are known·

Matico camphor,	Rubidium tartrate,
Patchouli camphor,	Cesium tartrate,
Laurel camphor,	Strychnine sulphate.[1]

It is interesting to compare in these substances the rotation in the crystalline form with that shown by an equally thick plate of the amorphous compounds (H. Traube). In the last case the action of the single molecules alone comes into play, while in the other the effect of a particular crystalline structure is to be added to this In this second case the molecular rotation and crystalline rotation must be added together, or, if they have opposite directions they may partially neutralize each other.

The following observations have been made on these substances

Matico camphor $C_{12}H_{20}O$.[2]—The rotation of the hexagonal trapezohedral-tetartohedral crystals was discovered by Hintze[3] and measured by him, and also, later by H. Traube.[4] The following angles were measured for a plate 1 mm. in thickness:

Hintze $\alpha_{Li} = -1.68°$, $\alpha_{Na} = -2.07°$, $\alpha_{Tl} = -2.47°$

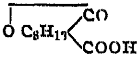
Traube· $\alpha_{Na} = -1.81°$, $-1.96°$, $-1.86°$

Mean, $\alpha_D = -1.92°$

Right rotating crystals have not yet been found.

H Traube[5] has measured the rotating power of the substance, which melts at 94°, in the liquid condition, in a tube 1 decimeter in length and at different temperatures, as follows:

Temp T	Rotation for 1 dm α_D	Sp gr at t° d^t_4.	Specific rotation $[\alpha]_D$.
108°	—26.29°	0.924	—28.45
115	—25.59	0.901	—28.40
126	—24.74	0.874	—28.32
135	—23.86	0.845	—28.24

[1] Recently W J. Pope (J Chem Soc, 69, 971) has added two bodies to this list. These are cis-π-camphanic acid,  $\overline{O\,C_8H_{13}}\!\left\langle\begin{matrix}CO\\COOH\end{matrix}\right.$, and transcamphotricarboxylic acid, $C_7H_{11}(COOH)_3$, described by Kipping J Chem. Soc., 69, 943 and 950. Data concerning the amount of rotation are not yet given,

[2] Kugler Ber d chem. Ges, 16, 2841

[3] Hintze Pogg Ann, 157, 127 (1876).

[4] Traube Sitzber, d Berliner Akad., 1, 195 (1895)

[5] H Traube Groth's Ztschr. f Kryst., 22, I, 47.

From the change in specific rotation with increasing temperature the specific rotation for the ordinary temperature (20°), may be calculated as approximately $[\alpha]_D = -29.1°$, Traube obtained almost the same value; that is, —28.7°, from observation of a 10 per cent. chloroform solution of the camphor. If we take $[\alpha]_D = -29°$ this represents the angle of rotation of a column of the amorphous camphor 100 mm. in length and having the ideal density of 1. If we reduce the rotation of the crystalline camphor, with a density of 1.08 at 15°, to the same standard we have:

$$[\alpha]_D = -\frac{1.92 \times 100}{1.08} = -178°$$

The angle of rotation of the amorphous and crystalline substances are related thus as 29 : 178, and if we assume that in the last number the molecular rotation is included, the part due to the crystalline structure must be 178°—29° = 149°. It follows therefore that the rotatory polarizing behavior of the crystals is about $\frac{1}{6}$ due to the molecular rotation and $\frac{5}{6}$ to the crystalline rotation.

Patchouli camphor, $C_{15}H_{26}O$.—The optical rotation of the hexagonal crystals, first noticed by v. Seherr-Thoss[1] was measured by H. Traube,[2] who found a rotation of $\alpha_D = -1.325°$ for 1 mm. Montgolfier[3] found $[\alpha]_D = -118°$ as the specific rotation of the fused substance at 59° (corresponding to about —118.3° for the ordinary temperature). From alcoholic solution in which the rotation decreases with the dilution he derived the value, $[\alpha]_D = -124.5°$ for the pure substance. From these two values, by taking the specific gravity as 1.051, according to Gal[4] (for the crystals), the rotation of a layer 1 mm. thick is calculated as $\alpha_D = 1.24$ and 1.31, which values agree very well with that observed in the crystals; *viz.*, 1.325. We have here a case in which the crystalline rotation coincides nearly with the molecular rotation, and one therefore in which the effect of the first is scarcely, if at all, perceptible.

Laurel camphor, $C_{10}H_{16}O$.—The crystals, according to H. Traube, hexagonal trapezohedral-tetartohedral, show, by the measurements of v. Seherr-Thoss[1] a right rotation as follows, for a plate of 1 mm. thickness ·

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[1] Private communication.

[2] H. Traube. Sitzungsber. der Berliner Akad., 1, 195 (1895).

[3] Montgolfier. Bull. soc. chim. [2], 28, 414 (1877).

[4] Gal. Ztschr. Chem., 220 (1869).

White light	Ray B	Ray D	Transition tint	Ray G
0 875°	0.455°	0.65°	0.73°	1.818°

From solutions of the camphor in different liquids the maximum specific rotation of the pure amorphous substance is found to be $[\alpha]_D = +55\ 5^\circ$;[2] therefore, if the specific gravity be taken as 0 998, the same as for the crystallized camphor, the angle of rotation for a layer of 1 mm. thickness is found to be $[\alpha]_D = +0.55^\circ$. This value is but little lower than that found for the crystals, $\alpha_D = +0\ 65^\circ$, from which it follows that the activity of the latter appears to depend almost wholly on the molecular rotation.

Right and left rubidium tartrate, $Rb_2C_4H_4O_6$.—According to H. Traube both salts are hexagonal trapezohedral-tetartohedral. As Wyrouboff[3] found and Traube[4] later the crystals formed from ordinary *d*- tartaric acid are left rotating, while those from *l*- tartaric acid are right-rotating. They observed for plates of 1 mm. thickness:

	d-Acid salt	*l*-Acid salt.
Wyrouboff..........	$\alpha_D = -10\ 7^\circ$	$\alpha_D = +10.5^\circ$
Traube	-10.24	$+10\ 12$

If the left-rotating crystals be dissolved in water the solution shows right rotation and *vice versa* The specific rotating power is diminished with increasing dilution, and at a rate which is shown, according to Rimbach,[5] by this formula, derived for the right rotating salt

$$[\alpha]_D^{20^\circ} = +25.63^\circ - 0\ 06123\, q,$$

in which q represents the percentage amount of water present. This formula was derived from observations on solutions containing up to 64 5 per cent. of the salt, and the constant, 25.63, may therefore be taken as satisfactorily representing the specific rotation of the amorphous anhydrous substance. Using with this the known specific gravity of the crystallized

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v Seherr Thoss Ztschr für Kryst, 23, 583 (1894)

[2] Mean of the determinations of Landolt Ann Chem. (Liebig), 189, 332, and Rimbach Ztschr phys Chem, 9, 698

[3] Wyrouboff. Jour de physik [3], 3, 451 (1894)

[4] H. Traube Sitzungsber. der Berliner Akad, 1, 195 (1895)

[5] Rimbach Ztschr phys Chem, 16, 671 (1895).

salt, $d = 2.694$, we obtain the rotation of a plate 1 mm. in thickness from

$$\alpha_D = 0\ 2563 \times 2\ 694 = +\ 0.69.$$

Regarding the phenomenon that the crystals show a rotation opposite in direction from that of the solutions it may be said that this depends on the activity of the molecules. It is well known that with many substances the direction of rotation is dependent on the concentration of their solutions. For example, malic acid, sodium malate and barium malate show a negative rotation in dilute solutions which decreases with increasing concentration, becomes zero (for malic acid in 34 per cent. solution) and then goes over into a right-hand rotation This would remain if the substances were finally brought to the solid condition. The same phenomenon is exhibited by solutions of *d*-tartaric acid, the specific rotation of which is given, according to Th Thomsen,[1] by this formula:

$$[\alpha]_D^{15} = -\ 1.265 + 0.1588\ q$$

According to this the point of inactivity is reached in a solution with 8 per cent. of water and the solid substance would show left rotation, as Biot[2] indeed found. The alkali tartrates, however, do not show this change of rotation, and also for the rubidium salt of dextrotartaric acid it is evident from the above formula of Rimbach that even in the most concentrated solution or in dry condition it can not exhibit left-hand rotation.

As, therefore, the activity of the molecules produces no change in the direction of rotation, it follows that in the structure of the crystals must be found the reason why these rotate oppositely from their solutions. Consequently it may be assumed that in the case of the rubidium salt of *d*-tartaric acid the observed rotation, $\alpha_D = -\ 10.24°$, is compounded from the molecular rotation, $\alpha_D = +\ 0.69°$, and a crystalline rotation amounting to $\alpha_D = -\ 10.93°$. The crystalline rotation would, therefore, be about sixteen times as great as the molecular.

Strychnine sulphate, $(C_{21}H_{22}N_2O_2)_2.H_2SO_4.6H_2O$.—In the tetragonal crystals rotation, left-handed, was first observed by

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[1] Thomsen · J. prakt Chem. [2], 32, 213

[2] Biot · Ann. chim. phys. [3], 28, 351.

Des Cloizeaux.[1] H. Traube[2] found $\alpha_D = - 13.25$ for 1 mm The solutions are also left-rotating. According to Wyrouboff[3] strychnine sulphate is not a true circularly polarizing substance It may be obtained in two forms, of which one is quadratic and optically inactive, while the other is built up of layers of clinorhombic plates. Light passing through these last crystals is partially elliptically polarized

Further, amylamine alum would belong also in the group if the statement of LeBel[4] is correct that it shows rotation in crystallized and dissolved form. But according to Wyrouboff[5] while the crystals show anomalous double refraction they are not circularly polarizing.

Finally it must be remarked that circular polarization should be expected in all those optically uniaxial and regular crystals of substances which exhibit molecular rotation The reason why this has been observed in but few cases up to the present time may be found in the fact that the rotating power of many bodies is too small to be detected in crystal plates, to which, on account of the necessary homogeneity and transparency, only a slight thickness can be given In conine aluminum alum $(C_8H_{17}N)_2.H_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, and in conine iron alum $(C_8H_{17}N)_2.H_2SO_4, + Fe_2(SO_4)_3 + 24H_2O$, which both crystallize regularly tetartohedral, H Traube[6] could find no evidence of circular polarization, even when, by piling up clear octahedra, layers of 1 to 3 cm. were obtained. In aqueous solution, however, optical activity was present, although small; for the aluminum salt, with $c = 46$, $[\alpha]_D = + 0.70°$ and for the iron salt, with $c = 66.8$ $[\alpha]_D = + 0.53°$ were found.

8. *Third Class.*—**Bodies which are active only in amorphous condition (natural liquids or solutions).**

The substances of this class are carbon compounds exclusively, no inorganic substances are known which belong here.

The following tables give a general summary of the active organic compounds with their optical modifications. Of the last the right-rotating are designated by +, the left-rotating by —, the racemic bodies, which may be split into their antipodes, by *r*, and the inactive forms, which can not be split up by *i*. The letter *i* is used also with some inactive bodies of unknown constitution, which on account of the connection are grouped with other substances. In the symbols, *d*(+), *d*(—), *l*(+), *l*(—), *d* and *l* indicate the derivation from a right- or left-rotating parent substance, while + and — indicate the direction of rotation.

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[1] Des Cloizeaux Pogg Ann, **102**, 477 (1857)

[2] H Traube Landolt-Boernstein's phys chem Tab, 2nd Ed p. 460.

[3] Wyrouboff Bull Soc Min., **7**, 10 (1884)

[4] Le Bel Ber d chem Ges, **5**, 391 (1872).

[5] Wyrouboff Ann chim phys [6], **8**, 340 (1886)

[6] H Traube · N Jahrb. fur Min, Beil, **9**, 625

For those bodies which have been studied in solution the solvent is mentioned, because this sometimes exerts an influence on the direction of rotation

W = water.
A = alcohol
E = ether
Ac = acetone
B = benzene.
C = chloroform.
Aa = acetic acid.
Bo = borax

f indicates that the body is in itself a liquid.

As far as space permits the constitutional formulas of the substances are given and in a manner which will indicate the asymmetric carbon atom, and that is by placing the four groups connected with it in parentheses.

The data on specific rotations will be given later in the section on constants of rotation.

1 *Hydrocarbons.*				
Methylethylpropylmethane, $(C_3H_7)(C_2H_5)C(H)(CH_3)$	*f*	+		
Diamyl, $(C_2H_5)(CH_3)(H)C(CH_2-CH_2)C(H)(CH_3)(C_2H_5)$	*f*	+		
Phenylamyl, $(C_6H_5CH_2)(C_2H_5)C(CH_3)(H)$	*f*	+		
Isobutylamyl, $(C_2H_5)(CH_3)C(H)(C_4H_9)$	*f*	+		
Ethylamyl, $(C_2H_5)(CH_3)C(H)(C_2H_5)$	*f*	+		
2. *Monohydric Alcohols and Derivatives*				
Methylethylcarbinol, $(C_2H_5)(CH_3)C(H)(OH)$	*f*		—	
Derivatives: chloride, iodide	*f*	+		
Amyl alcohols:				
Methylethylcarbincarbinol, common active amyl alcohol, $(C_2H_5)(CH_3)C(H)(CH_2OH)$	*f*	+	—	*r*

Derivatives: (*a*) From *l*-amyl alcohol: chloride, bromide, iodide, cyanide, sulphydrate, thiocyanate, ether, ester, amylsulphuric acid, diamylamine, triamylamine and salts of amylamine		+			
Amylamine			—		
(*b*) From *d*-amyl alcohol iodide	*f*		—		
Methylpropylcarbinol, $(C_3H_7)(CH_3)C(H)(OH)$	*f*		—	*r*	
Derivatives From the *l*-alcohol: chloride, iodide	*f*	+			
Acetin, propin, butyrin	*f*		—		
Hexyl alcohols					
Methylethylpropyl alcohol, $(C_2H_5)(CH_3)C(H)(CH_2CH_2OH)$	*f*	+			
Ethylpropylcarbinol, $(C_3H_7)(C_2H_5)C(H)(OH)$	*f*	+		*r*	
Derivatives Chloride	*f*		—		
Iodide	*f*	+			
Methylbutylcarbinol, $(C_4H_9)(CH_3)C(H)(OH)$	*f*		—	*r*	
Methylamylcarbinol, $(C_5H_{11})(CH_3)C(H)(OH)$	*f*	+		*r*	

3 *Dihydric Alcohols and Derivatives.*

Propyleneglycol, $(CH_3)(H)C(OH)(CH_2OH)$	*f*	+	—	*r*	
Derivatives From *l*-propyleneglycol propylene-oxide	*f*	+			
Diacetin, mono- and dichlorhydrin, Chlorbromhydrin	*f*	+			
Chloracetin, chlorbutyrin	*f*		—		
Diphenylglycol				*r*	
Derivative Diphenylethylenediamine, $[(C_6H_5)(NH_2)(H)C]_2$	*E*	+	—	*r*	

4 *Trihydric and Tetrahydric Alcohols and Derivatives.*

No optically active compounds are known.

5 *Pentahydric Alcohols*

Arabitol, $C_5H_{12}O_5$	*W* + *Bo*		—		
Xylitol, $C_5H_{12}O_5$	*W* (+ *Bo*)	+?			*i*
Adonitol, $C_5H_{12}O_5$	*W* (+ *Bo*)				*i*
Rhamnitol, $C_6H_{14}O_5$	*W*	+			
Quercitol, $C_6H_{12}O_5$ (cyclic)	*W*	+			

6 *Hexahydric Alcohols.*

d-Mannitol, $C_6H_{14}O_6$	*W*		—	?	
	W + *Bo* and other salts	+			
	alkalies		—		
l-Mannitol, $C_6H_{14}O_6$	*W* + *Bo*		—		

Derivatives · From *d*-mannitol, isomannitol (*W*, *A*.), β-mannitol (*W*), hexaacetate (*W*), hexachloride (*B*)		+			
Mannitoldichlorhydrin (*W*)			—		
d-Sorbitol, $C_6H_{14}O_6$	*W*		—		*i*
	W + *Bo*, alkalies	+			
l-Sorbitol, $C_6H_{14}O_6$	*W* + *Bo*		—		
d-Iditol, $C_6H_{14}O_6$	*W*	+			
l-Iditol $C_6H_{14}O_6$	*W*		—		
Dulcitol, $C_6H_{14}O_6$	*W*				
Talitol, $C_6H_{14}O_6$	*W*				*i*
Rhamnohexitol, $C_7H_{16}O_6$	*W*	+			
d-Inositol, $C_6H_{12}O_6$ (cyclic)	*W*	+			
Hexaacetate	*A*	+			
l-Inositol	*W*		—		
Hexaacetate	*A*		—		
i-Inositol	*W*			*r*	
Bornesitol, methyl inositol, $C_7H_{14}O_6$ (cyclic)	*W*	+			
Pinitol, $C_7H_{14}O_6$ (cyclic)	*W*	+			
Quebrachitol, $C_7H_{14}O_6$ (cyclic)	*W*		—		

7 *Heptahydric Alcohols*

Volemitol, $C_7H_{16}O_7$	*W*	+			
α-Glucoheptitol, $C_7H_{16}O_7$	*W*				*i*
α-Galaheptitol, $C_7H_{16}O_7$	*W*	?	?		
d-Mannoheptitol, $C_7H_{16}O_7$	*W*				
	W + *Bo*	+			
l-Mannoheptitol, $C_7H_{16}O_7$	*W*		?		
i-Mannoheptitol, $C_7H_{16}O_7$	*W*			*r*	

8 *Octahydric Alcohols*

d-Mannooctitol, $C_8H_{18}O_8$	*W*	?			
l-Glucooctitol, $C_8H_{18}O_8$	*W*	+			

9 *Nonahydric Alcohols*

Glucononitol, $C_9H_{20}O_9$		?			

10 *Acids with Two Atoms of Oxygen, and Derivatives*

Valeric acid, $(C_2H_5)(CH_3)C(H)(COOH)$	*f*	+	—	*r*	
Derivatives From *d*-valeric acid ester, valeraldehyde, valeryl chloride	*f*	+			
Caproic acid, $(C_2H_5)(CH_3)C(H)(CH_2COOH)$	*f*	+			
Derivative Hexylester	*f*	+			

11 *Acids with Three Atoms of Oxygen and Derivatives.*

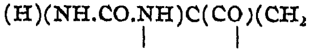
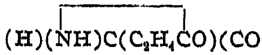
Ethylidene lactic acid, $(CH_3)(H)C(OH)(COOH)$	*W*	+	—	*r*	

Derivatives: From *d*-(sarco)lactic acid salts, esters, anhydride (alanin?)	*W*		—	
From *l*-lactic acid: salts, esters, anhydride	*W*	+		
α-Oxybutyric acid, $(C_2H_5)(H)C(OH)(COOH)$	*W*	+	—	*r*
β-Oxybutyric acid, $(CH_3)(H)C(OH)(CH_2COOH)$	*W*		—	*r*
Phenylglycolic acid, $(C_6H_5)(H)C(OH)(COOH)$	*W*	+	—	*r*
Isopropylphenylglycolic acid, $(C_6H_5)(C_3H_7)C(OH)(COOH)$	*W*	+	—	*r*
Tropic acid, $(C_6H_5)(H)C(CH_2OH)(COOH)$	*W*	+	—	*r*
α-Amido propionic acid, alanin, $(CH_3)(H)C(NH_2)(COOH)$	*W*		?	
Phenyl-α-amidopropionic acid, $(CH_3)(H)C(NHC_6H_5)(COOH)$	*W*		—	*r*
α-Amidocaproic acid, leucine, $(C_4H_9)(H)C(NH_2)(COOH)$	*W*	+	—	*r*
	acids or alkalies	—	+	
Derivatives: Phthalylleucine, leucinephthalic acid.			—	*r*
Cystin, $(CH_3)(SH)C(NH_2)(COOH)$	*W*, HCl		—	
Derivatives: Phenyl cystin, $(CH_3)(C_6H_5S)C(NH_2)(COOH)$	*W*, NaOH		—	
Bromphenyl cystin	*W*, NaOH		—	
Phenyl mercapturic acid, $(CH_3)-(C_6H_5S)C-(NHCOCH_3)(COOH)$	*A*		—	
Bromphenyl mercapturic acid	*A*		—	
Sodium salt of same	*W*	+		
Oxyphenyl alanin, tyrosin, $(HO\ C_6H_4\ CH_2)(H)C(NH_2)(COOH)$	*W*, NaOH, HCl	+	—	*r*
Parasorbic acid, $(C_2H_5)(H)C(O)(CH{=}CH-CO)$	*f*	+		
Ricinoleic acid, $(C_6H_{13})(H)C(OH)(CH\ C\ C_8H_{16}.COOH)$	*f*, *Ac*	+		
Ricinelaidic acid, (isomeric with ricinoleic acid)	*Ac*, *A*	+		
Ricinstearolic acid, $C_{17}H_{30}.OH\ COOH$	*Ac*	+		

12. *Acids with Four Atoms of Oxygen and Derivatives.*

Pyrotartaric acid, $(CH_3)(H)C(COOH)(CH_2.COOH)$	*W*	+	—	*r*
Glyceric acid, $(CH_2OH)(H)C(OH)(COOH)$	*W*	+	—	*r*
Derivatives: Salts and esters of the *d*-acid	*W*		—	
Phenyl-α-bromlactic acid, $(C_6H_5)(H)(OH)C-C(Br)(H)(COOH)$	*W*	+	—	*r*
Phenyloxyacrylic acid, $(C_6H_5)(H)(O)C-C(O)(H)(COOH)$, salts	*W*	+	—	
Phenyldibrompropionic acid, cinnamic acid dibromide, $(C_6H_5)(H)(Br)C-C(Br)(H)(COOH)$	*A*	+	—	*r*
Phenyldibrombutyric acid, $(C_6H_5)(H)(Br)C-C(Br)(H)(CH_2COOH)$	*A*	+	—	*r*

13. *Acids with Five Atoms of Oxygen and Derivatives.*

Trioxybutyric acid, $(CH_2OH)(H)(OH)C-C(H)(OH)(COOH)$	*W*	+			
Shikiminic acid, $C_7H_{10}O_5$ (cyclic)	*A*		—		
Derivatives: Triacetyl, propionyl, butyryl esters, hydroshikiminic acid, dibromshikiminic acid	*W*		—		
Bromshikiminic acid lactone	*W*	+			
Dioxyhydroshikiminic acid	*W*				*i*
Malic acid, $(H)(OH)C(COOH)(CH_2COOH)$	*W*	+	—	*r*	
d-Malic acid, according to concentration	*W*	+	—		
anhydrous			—		
l-Malic acid, (common acid) according to concentration	*W*	+	—		
anhydrous		+			
Derivatives: Of *l*-malic acid: malates, esters, amide	*W*		—		
Acetylmalic acid	*W*, *Ac*		—		
Acetylmalic acid anhydride	*f*, *Ch*		—		
Propionyl-, butyrylmalic acid, and anhydride	*Ch*		—		
Methylmalic acid, $(CH_3)(COOH)(H)C-C(OH)(H)(COOH)$	*W*	+	—		
Chlorsuccinic acid, $(Cl)(H)C(COOH)(CH_2COOH)$	*W*	+			
Methoxysuccinic acid, $(CH_3O)(H)C(COOH)(CH_2COOH)$	*W*	+	—	*r*	
Ethoxysuccinic acid	*W*	+	—	*r*	
Urimidosuccinic acid,  $(H)(NH.CO.NH)C(CO)(CH_2COOH)$	*W*	+	—		
Uramidosuccinamide, $(H)(CH_2.CO.NH_2)C(NH\,CO\,NH_2)(COOH)$	*W*	+	—		
Aspartic acid, $(H)(NH_2)C(COOH)(CH_2COOH)$	*W*	+	—	*r*	
Common aspartic acid, in alkaline solution —, in acid solutions +.					
β-Asparagin, $(H)(NH_2)C(COOH)(CH_2.CONH_2)$	*W*	+	—		
l-Asparagin, in alkaline solution —, in acid solution +.					
Oxyglutaric acid, $(H)(OH)C(COOH)(C_2H_4.COOH)$	*W*		—	*r*	
Glutaminic acid, $(H)(NH_2)C(COOH)(C_2H_4.COOH)$	*W*, acids	+	—	*r*	
d-Acid	*W* + alkalies		—		
d-Amide	HCl	+			
Pyroglutaminic acid,  $(H)(NH)C(C_2H_4CO)(COOH)$, and amide	*W*	+	—	*r*	
α-Isotrioxystearic acid, $C_{17}H_{32}(OH)_3COOH$			—		

14. *Acids with Six Atoms of Oxygen and Derivatives.*

[The aldehydes of these monobasic acids are described as oxyaldehydes (sugars) below.]

Tartaric acid, (COOH)(OH)(H)C—C(H)(OH)(COOH)	*W*	+	—	*r*
Derivatives Of *d*-tartaric acid: neutral and acid salts, esters, methyl and ethyl tartaric acid salts, tartramide	*W*	+		
Diacetyl tartaric acid anhydride and diethyl, dipropyl (*Ac*, *A*), dibutyl ester, di-benzoyl tartaric acid anhydride (*Ac*)		+		
Diacetyl tartaric acid and salts, diacetyl tartaric acid dimethyl, dibenzoyl tartaric acid hydrate, dimethyl, diethyl, and dibutyl esters	*A*		—	
Derivatives Of *l*-tartaric acid neutral and acid salts, amide	*W*		—	
Diacetyl tartaric acid dimethyl ester	*A*	+		
Arabonic acid, $C_5H_{10}O_6$; lactone, $C_5H_8O_5$	*W*		—	
Ribonic acid, $C_5H_{10}O_6$, lactone, $C_5H_8O_5$	*W*		—	
Cadmium salt	*W*	+		
Rhamnonic acid, $C_6H_{12}O_6$, lactone	*W*		—	
Xylonic acid, $C_5H_{10}O_6$	first —, then	+		
Strontium salt	*W*	+		
Lyxonic acid, $C_5H_{10}O_6$	*W*	+		
Saccharinic acid, $C_6H_{12}O_6$, lactone (saccharin)	*W*	+		
Sodium and calcium salts	*W*	—		
Isosaccharinic acid, $C_6H_{12}O_6$, lactone (isosaccharin)	*W*	+		
Sodium salt	*W*		—	
Anilide	*A*			*r*
Metasaccharinic acid, $C_6H_{12}O_6$, lactone (metasaccharin)	*W*		—	
Quinic acid, $C_7H_{12}O_6$ (cyclic)	*W*		—	*r*
Chitaric acid, $C_6H_{10}O_6$	?	+		

15 *Acids with Seven Atoms of Oxygen and Derivatives.*

[For aldehydes see under oxyaldehydes (sugars).]

Trioxyglutaric acid (from arabinose) $(COOH)_2.(CHOH)_3$	*W*		—	
Potassium salt	*W*	+		
Saccharonic acid, (COOH)(OH)(H)C—C(H)(OH)—C(CH_3)(OH)(COOH), lactone	*W*		—	
d-Gluconic acid, $C_6H_{12}O_7$, calcium salt, lactone	*W*	+		
l-Gluconic acid, $C_6H_{12}O_7$, calcium salt.	*W*		—	
i-Gluconic acid, $C_6H_{12}O_7$	*W*			*r*
Glucoronic acid, $C_6H_{10}O_7$	*W*	+		

Derivatives: Thymol- and dichlorthymolglucoronic acid	?		—		
d-Gulonic acid, $C_6H_{12}O_7$, lactone	*W*	+			
l-Gulonic acid, $C_6H_{12}O_7$; lactone	*W*		—		
Phenylhydrazide	*W*	+			
i-Gulonic acid, $C_6H_{12}O_7$	*W*			*r*	
d-Mannonic acid, $C_6H_{12}O_7$; lactone	*W*	+			
l-Mannonic acid, $C_6H_{12}O_7$, lactone	*W*		—		
i-Mannonic acid	*W*			*r*	
d-Idonic acid, $C_6H_{12}O_7$, cadmium salt + cadmium bromide	*W*	+			
l-Idonic acid, $C_6H_{12}O_7$; cadmium salt + cadmium bromide	*W*		—		
d-Galactonic acid, $C_6H_{12}O_7$; lactone	*W*		—		
Derivative: Calcium salt	*W*	+			
l-Galactonic acid, $C_6H_{12}O_7$; lactone	*W*	+			
i-Galactonic acid, $C_6H_{12}O_7$	*W*			*r*	
Talonic acid, $C_6H_{12}O_7$	*W*	+			
α-Rhamnohexonic acid, $C_7H_{14}O_7$; lactone	*W*	+			
β-Rhamnohexonic acid, $C_7H_{14}O_7$; lactone	*W*	+			
Chitaminic acid, $C_6H_{11}(NH_2)O_6$	?	+			
Oxygluconic acid, $C_6H_{10}O_7 + 2H_2O$	*W*		—		

16. *Acids with Eight Atoms of Oxygen and Derivatives*

Dibasic acids (tetroxyadipic acids)

d-Saccharic acid, $C_6H_{10}O_8$, lactone, ammonium-, potassium salt	*W*	+			
l-Saccharic acid, $C_6H_{10}O_8$; potassium salt	*W*		—		
i-Saccharic acid, $C_6H_{10}O_8$	*W*			*r*	
Isosaccharic acid, $C_6H_{10}O_8$, diethyl ester, diamide	*W*	+			
d-Mannosaccharic acid, $C_6H_{10}O_8$, lactone, $C_6H_6O_6$	*W*	+			
l-Mannosaccharic acid, $C_6H_{10}O_8$, lactone	*W*		—		
i-Mannosaccharic acid, $C_6H_{10}O_8$	*W*			*r*	
d-Idosaccharic acid, $C_6H_{10}O_8$	*W*	+			
l-Idosaccharic acid, $C_6H_{10}O_8$	*W*		—		
Mucic acid, $C_6H_{10}O_8$	*W*				*i*
Allomucic acid, $C_6H_{10}O_8$	*W*				
d-Talomucic acid, $C_6H_{10}O_8$	*W*	+			
l-Talomucic acid, $C_6H_{10}O_8$	*W*		—		

Monobasic acids (heptonic acids).

α-Glucoheptonic acid, $C_7H_{14}O_8$; lactone	*W*		—		
β-Glucoheptonic acid, $C_7H_{14}O_8$; lactone	*W*		—		
d-Galactosecarboxylic acid, $C_7H_{14}O_8$; barium salt	*W*	+			
d-Fructosecarboxylic acid, $C_7H_{14}O_8$; lactone	*W*	+			
d-Mannoheptonic acid, $C_7H_{14}O_8$ and lactone	*W*		—		

l-Mannoheptonic acid, $C_7H_{14}O_8$; lactone	*W*	+			
i-Mannoheptonic acid, $C_7H_{14}O_8$	*W*			*r*	
Rhamnoheptonic acid, $C_8H_{16}O_8$; lactone	*W*	+			

17. *Acids with More Than Eight Oxygen Atoms and Derivatives*

Dibasic acids.

β-Glucopentoxypimelic acid, $C_7H_{12}O_9$, lactone acid	*W*	+			
α-Glucopentoxypimelic acid, $C_7H_{12}O_9$	*W*				*i*

Monobasic acids

α-Glucooctonic acid, $C_8H_{16}O_9$, lactone	*W*	+			
β-Glucooctonic acid, $C_8H_{16}O_9$, lactone	*W*	+			
Rhamnooctonic acid, $C_8H_{16}O_9$, lactone	*W*		—		
d-Mannooctonic acid, $C_8H_{16}O_9$; lactone	*W*		—		
α-Glucononpremise acid, $C_9H_{18}O_{10}$, mixed with lactone	*W*	+			
d-Mannononpremise acid, $C_9H_{18}O_{10}$; lactone	*W*		—		

18. *Oxyaldehydes, Aldoses, Aldehyde Sugars*

(*a*) *Pentoses*

l-Arabinose, $C_5H_{10}O_5$	*W*	+			
Derivatives: Osone, tetracetate (*A*), diacetone, benzylarabinoside (*W*),		+			
β-Arabinochloral, $C_7H_6Cl_3O_5$	*W*		—		
Phenylosazone (*A*) beginning		+	then		*i*
d-Arabinose, $C_5H_{10}O_5$	*W*		—		
i-Arabinose, $C_5H_{10}O_5$				*r*	
Rhamnose, $C_6H_{12}O_5$	*W*	+			
	A		—		
Derivatives: Phenylhydrazone, oxime	*W*	+			
Ethyl-, methylrhamnoside	*A*		—		
Fucose, $C_6H_{12}O_5$	*W*		—		
Xylose, $C_5H_{10}O_5$	*W*	+			
Derivatives *α*-Methylxyloside.	*W*	+			
β-Methylxyloside, xylochloral, osazone	*A*		—		
Lyxose, $C_5H_{10}O_5$	*W*		—		

(*b*) *Hexoses*

d-Glucose, $C_6H_{12}O_6$	*A*, *W*	+			
Derivatives *α*-Methyl- and *α*-ethylglucoside (*W*), Chloralose [$C_8H_{11}Cl_3O_6$] (*A*, alkalies), acetochlorhydrose [$C_6H_7OCl(C_2H_3O_2)_4$], octoacetate, (*B*), pentacetate (*C*), glucoseammonia (*W*)		+			

Mercaptal (*W*), diacetone, phenylhydrazone (*W*), osazone (*Aa*), osone (*W*), oxime (*W*), dextroseamidoguanidine hydrochloride (*W*), anilide and toluidide (*A*), anhydroglucose-levoglucosan			—		
l-Glucose, $C_6H_{12}O_6$	*W*		—		
Derivatives: α-Methylglucoside	*W*		—		
Osazone	*Aa*	+			
i-Glucose, $C_6H_{12}O_6$	*W*			*r*	
Glucosamine, $C_6H_{11}O_5NH_2$, salts,	*W*	+			
Isoglucosamine, $C_6H_{11}O_5NH_2$ salts,	*W*		—		
d-Gulose, $C_6H_{12}O_6$	*W*		?		
l-Gulose, $C_6H_{12}O_6$ sirup,	*W*	+			
i-Gulose, $C_6H_{12}O_6$	*W*			*r*	
d-Mannose, $C_6H_{12}O_6$	*W*	+			
Derivatives: Oxime	*W*	+			
Phenylhydrazone (*W* + HCl), osazone	(*Aa*)		—		
l-Mannose, $C_6H_{12}O_6$ sirup	*W*		—		
Derivatives: Phenylhydrazone (*W* + HCl), osazone	(*Aa*)	+			
i-Mannose, $C_6H_{12}O_6$	*W*			*r*	
d-Galactose, $C_6H_{12}O_6$	*W*	+			
Derivatives: Oxime (*W*), α-methylgalactoside (*W*), β-methylgalactoside (*W* + borax) ethylgalactoside (*W*), pentacetate (*C*)		+			
Anilide, toluidide, phenylhydrazone	*A*		—		
Mercaptal	*W*		—		
Osazone					*i*
l-Galactose, $C_6H_{12}O_6$	*W*		—		
Derivatives: Phenylhydrazone	*W*	+			
Osazone	?				*i*
i-Galactose, $C_6H_{12}O_6$	*W*			*r*	
Talose, $C_6H_{12}O_6$	*W*	+		*r*	
Sorbose, $C_6H_{12}O_6$	*W*		—		
Derivative Methylsorboside	*W*		—		
Idose, $C_6H_{12}O_6$	*W*	+?	+?	*r*	
Rhamnohexose, $C_7H_{14}O_6$	*W*		—		
c) *Heptoses:*					
α-Glucoheptose, $C_7H_{14}O_7$	*W*		—		
Mannoheptose, $C_7H_{14}O_7$	*W*	+	—	*r*	
Rhamnoheptose, $C_8H_{16}O_7$	*W*	+			
d) *Octoses:*					
α-Glucooctose, $C_8H_{16}O_8$	*W*	+	—		
d-Mannooctose, $C_8H_{16}O_8$ sirup	*W*	+			

e) Nonoses

Gluconononose, $C_9H_{18}O_9$	sirup *W*	+		
Mannononose, $C_9H_{18}O_9$	*W*		—	

19. *Oxyketones, Ketoses, Ketone Sugars.*

d-Fructose, levulose, $C_6H_{12}O_6$	*W*		—	
Derivatives. Oxime, anilide (*A*), osazone (*Aa*)			—	
pentacetate	*C*	+		
l-Fructose, $C_6H_{12}O_6$	*W*	+		
Derivative: Osazone	*Aa*	+		
i-Fructose, α-acrose, $C_6H_{12}O_6$				*r*
Invert sugar = *d*-glucose (dextrose) + *d*-fructose (levulose)	*W*		—	

20 *Disaccharides*, $C_{12}H_{22}O_{11}$.

Cane sugar	*W*	+
Milk sugar (+ H_2O)	*W*	+
Maltose (+ H_2O)	*W*	+
Isomaltose	*W*	+
Trehalose (mycose) (+ 2 H_2O)	*W*	+
Melebiose	*W*	+
Turanose	*W*	+
Lupeose	*W*	+
Cyclamose	*W*	—
Agavose	*W*	*i*

21 *Trisaccharides*, $C_{18}H_{32}O_{16}$

Meletriose, raffinose (+ 5 H_2O)	*W*	+*i*
Melezitose (+ $2H_2O$)	*W*	+

22. *Polysaccharides.*

Gentianose, $C_{36}H_{62}O_{31}$?	*W*	+
Lactosin, $C_{36}H_{62}O_{31}$?	*W*	+
Stachyose, ?	*W*	+

23 *Carbohydrates*, $(C_6H_{10}O_5)_n$.

Amorphous soluble starch	*W*	+
Crystallized soluble starch, amylodextrine	*W*	+
Achrodextrine	*W*	+
Maltodextrine	*W*	+
Wood dextrine	*W*	+
Fermentation gum, dextrane	*W*	+
γ-Galactan	*W*	+
α-Galactan	*W*	+
Glycogen	*W*	+
Fermentation mucin	*W*	+
Cellulosin	*W*	+
Cellulose (CuO-ammonia, HCl)		—
α and β Amylan	*W*	—
Gelose	*W* + acids	—
Graminin	*W*	—
Inulin	*W*	—
Irisin	*W*	—
Levosin	*W*	—
Levosan	*W*	—
Sinistrin	*W*	—
Triticin	*W*	—
Levulin (synanthrose)	*W*	*i*

24 *Gums*

Arabin, arabic acid	*W*	±
Wood gum, xylan	*W*	—
Vegetable mucilage	*W*	+
Wine gum	*W*	+

25 *Pectin Bodies* *W*, +, —, *i*

26. *Alcohols and Acids of Unknown Structure*

Quebrachol, $C_{20}H_{34}O$	*C*	—
Cupreol, " " "	*A*	—
Cinchol, " " "	*C*	—
Cholestol, $C_{22}H_{38}O$	*A*	—
Cholesterin, $C_{26}H_{44}O$	*A*	—
Phytocholesterin, $C_{26}H_{44}O$	*A*	—
Isocholesterin, " " "	*E*	+
Paracholesterin, " " "	*C*	—
Caulosterin, " " "	*C*	—
Quinovic acid, $C_{32}H_{48}O_6$, K-salt	*W*	+
Quinaethonic acid, $C_{14}H_{18}O_9$	*W*	—
Atractylic acid, $C_{30}H_{54}S_2O_{18}$, K-salt	*W*	—

27. *Terpenes*, $C_{10}H_{16}$.

1. *Pinene* (Australene +, Terebenthene —)	*f*	+	-
Hydrochloride, $C_{10}H_{16}HCl$	*A*	*d* (+)	*l* (
Hydrobromide, $C_{10}H_{16}HBr$	*A*		*l* (
d-Dibromide, $C_{10}H_{16}Br_2$	*f*	*d* (+)	
d-Nitrosochloride, $C_{10}H_{16}NOCl$	*C*		
l-Aldehyde, $C_{10}H_{14}O$	*f*		*l* (
2 *Camphene*	*A*	+	-
l-Hydrochloride, $C_{10}H_{16}HCl$	*A*		*l* (
α- and β-Camphene phosphonic acids, $C_{10}H_{15}H_2PO_3$	*A*		*l* (
3. *Fenchene*	*f*		
4 *Limonene*	*f*	+	—
Hydrochloride, $C_{10}H_{16}HCl$	*f*	*d* (+)	*l* (-
Tetrabromide, $C_{10}H_{16}Br_4$	*C*	*d* (+)	*l* (-
α-Nitrosochloride, $C_{10}H_{16}NOCl$	*C*	*d* (+)	*l* (-
β- " " " " "	*C*	*d* (+)	*l* (-
α-Benzoyl nitrosochloride, $C_{10}H_{16}NOCl\ C_7H_5O$	acetic ether	*d* (+)	*l* (-
d-β-Benzoyl nitrosochloride, $C_{10}H_{16}NOCl\ C_7H_5O$	acetic ether	*d* (+)	
α-Nitrolpiperidine, $C_{10}H_{16}NO\ NC_5H_{10}$	*C*	*d* (+)	*l* (—
β-Nitrolpiperidine, $C_{10}H_{16}NO\ NC_5H_{10}$	*C*	*l* (+)	*d* (—
α-Nitrolanilide, $C_{10}H_{16}\ NO\ NH\ C_6H_5$	*C*	*d* (+)	*l* (
β-Nitrolanilide, $C_{10}H_{16}\ NO\ NH.C_6H_5$	*C*	*l* (+)	*d* (—
Nitroso-α-nitrolanilide, $C_{10}H_{16}NO.N(NO)C_6H_5$	*C*	*d* (+)	*l* (—
Nitroso-β-nitrolanilide, $C_{10}H_{16}NO\ N(NO)C_6H_5$	*C*	*l* (+)	
α-Nitrolbenzylamine, $C_{10}H_{16}NO\ NHC_7H_7$	*C*	*d* (+)	*l* (—
" " " hydrochloride and nitrate		*d* (+)	*l* (+
d-Limonene-α-nitrolbenzylamine-*d*-tartrate	*W* + *A*		—
l- " " " " *l*	*W* + *A*	+	
d- " " " " *l*	*W* + *A*		-
l- " " " " *d*	*W* + *A*	+	
Carvoxime, $C_{10}H_{14}NOH$, from α- and β-nitrosochloride	*A*	*l* (+)	*d* (—
Benzoylcarvoxime, $C_{10}H_{14}NO.COC_6H_5$	*C*	*l* (+)	*d* (—
5 *Sylvestrene*	*f*	+	
Dihydrochloride, hydrobromide, tetrabromide, nitrolbenzylamine	*C*	+	
6. *Phellandrene*	*f*	*d* (+)	*l* (—)
Nitrite, $C_{10}H_{16}N_2O_3$	*C*	*l* (+)	*d* (—)
7. *Isoterpene*	*f*	+	—
8. *Terpenene*	*f*		

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[1] Dipentene.

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9 *Terpinolene and tetrabromide*	*f*				
Cadinene, $C_{15}H_{24}$ (and hydrochloride, bromide, iodide)	*C*		—		*i*
Patchouline, $C_{15}H_{24}$	*B*		—		
α- and β-Amyrilene, $C_{30}H_{48}$	*B*	+			
Tetraterebenthene, $C_{40}H_{64}$	*f*		—		
Menthene, $C_{10}H_{18}$	*f*	+	—		
Menthonaphthene, $C_{10}H_{20}$	*f*				*i*
28 *Camphors and Derivatives.*					
Menthol, $C_{10}H_{19}OH$	*A*	+	—		
Menthylamine, $C_{10}H_{19}NH_2$	*f*	*d* (+)	*l* (—)		
" hydrochloride, bromide, iodide	*W*	*d* (+)	*l* (—)		
Formyl, acetyl, propionyl, butyryl menthylamine	*C*	*d* (+)	*l* (—)		
l-Menthylesters of benzoic, succinic and phthalic acids	*B*		*l* (—)		
l-Menthylcarbonate, $(C_{10}H_{19})_2CO_3$	*B*		*l* (—)		
l-Menthylurethane, $C_{10}H_{19}O$ CO NH_2	*C*		*l* (—)		
Menthone, $C_{10}H_{18}O$	*f*	*d* (+)	*l* (—)		
Menthoneoxime, $C_{10}H_{18}$ NOH and hydrochloride	*A*	*d* (+)	*l* (—)		
Iso-*l*-menthoneoxime, $C_{10}H_{18}NOH$	*A*		*l* (—)		
Menthonitrile, $C_9H_{17}CN(f)$	*A*		*l* (—)		
Terpine, $C_{10}H_{18}(OH)_2$ and hydrate (+ H_2O)	*f*				*i*
Terpineol, $C_{10}H_{17}(OH)$	*f*	+	—		*i*
Cineol (eucalyptol, cajeputol), $C_{10}H_{18}O$	*f*				*i*
α-*Borneol* (α-camphol), $C_{10}H_{17}OH$, Borneo-camphor +, valerian camphor—	*A*	+	—	*r*	
Ethylborneol, $C_{10}H_{17}OC_2H_5$	*f*	*d* (+)			
Bornylchloride, $C_{10}H_{17}Cl$, bornylamine, $C_{10}H_{17}NH_2$	*A*		*d* (—)		
Bornyl acetate, benzoate, neutral and acid succinate, neutral and acid phthalate, carbonate	*A*	*d* (+)	*l* (—)	*r*	
Bornyl phenylurethane (toluene)		*d* (+)	*l* (—)	*r*	
Chloral bornylate$(C_{10}H_{17}O)(H)C(OH)(CCl_3)$ }	*B*	*d* (+)	*l* (—)	*r*	
Bromal bornylate }					
β-Borneol (β-camphol), isocamphol, from *d*- and *l*- camphor	*A*	*d* (—)	*l* (—)		
Pinol, sobrerone, $C_{10}H_{16}O$	*f*				*i*
Pinol hydrate, sobrerol, $C_{10}H_{16}O.H.OH$	*A*	*d* (+)	*l* (—)	*r*	
Camphor, $C_{10}H_{16}O$, laurel camphor +, matricaria camphor—,	*A*	*d* (+)	*l* (—)	*r*	

Derivatives from d- and l-camphor ·				
Camphoroxime, $C_{10}H_{16}NOH$	*A*	*l* (+)	*d* (−)	
Camphoroxime hydrochloride, $C_{10}H_{16}NOH.HCl$	*A*	*l* (−)	*d* (−)	
α-Camphor sulphochloride, $C_{10}H_{15}OSO_2Cl$...	*C*	*d* (−)	*l* (−)	
Benzalcamphor, $C_{10}H_{14}O\ C_7H_6$, benzylcamphor, $C_{10}H_{15}O\ C_7H_7$.....................	*A*	*d* (+)	*l* (−)	*r*
Derivatives of d-camphor ·				
α-Nitrocamphor, $C_{10}H_{15}NO_2$..............*B*,	*A*		—	
Salts ....*W*,	*A*	—		
β-Nitrocamphor, $C_{10}H_{15}NO_2$	*A*	—		
" "	*B*		—	
α-Chlornitrocamphor, $C_{10}H_{14}ClONO_2$........	*A*		—	
β- " " " "	*A*	—		
Bromnitrocamphor, $C_{10}H_{14}BrONO_2$..	*A*		—	
α-Nitrosocamphor, $C_{10}H_{15}O\ NO$.	*B*	—		
α- and β-Mono- and dichlorcamphor, trichlorcamphor	*C*	+		
α- and β- Bromcamphor, $C_{10}H_{15}BrO$	*A*	—		*r*
α- and β-Chlorbromcamphor, $C_{10}H_{14}ClBrO$, Iod camphor, $C_{10}H_{15}IO$	*C*	—		
Camphor sulphonic acid, $C_{10}H_{15}O\ HSO_3$	*W*			
Camphor sulphonamide, $C_{10}H_{15}O\ SO_2.NH_2$..	*C*	—		
α-Chlorcamphor sulphonic acid, $C_{10}H_{14}ClO\ HSO_3$, ...	*W*	—		
Salts	*W*	—		
α-Chlorcamphor sulphonchloride, $C_{10}H_{14}ClO,SO_2Cl$ ....*C*,	*A*	+		
α-Chlorcamphor sulphonamide, $C_{10}H_{14}ClO\ SO_2NH_2$..........	*A*	—		
α- and β-Bromcamphor sulphonic acid and salts	*A*	—		
α-Bromcamphor sulphonchloride and amide *C*,	*A*	+		
Cyancamphor, $C_{10}H_{15}OCN$, cyanmethyl, ethyl, propyl and benzyl camphor..............	*B*	+		
Methyl camphor, $C_{10}H_{15}\ OCH_3$ and ethyl camphor..............	*A*	+		
Compounds of camphor with chloral, chloral-hydrate and chloral alcoholate.....	*A*	+		
Compounds of camphor with phenol, α- and β-naphthol, resorcinol, salicylic acid........	*A*	—		
Camphinic acid, $C_{10}H_{16}O_2$, campholic acid, $C_{10}H_{18}O_2$ and cyancampholic acid.........	*A*	+		
Oxycamphocarbaminic acid, $C_{10}H_{16}O.NH_2\ COOH$.................................	*A*	+		
Methyl hydroxycamphocarboxylic acid, $C_{10}H_{16}O_2\ CH_3.COOH$................... ..	*A*	+		

Camphoric acids, $C_{10}H_{16}O_4$, *d* from laurel camphor, *l* from matricario camphor	*A*	*d* (+)	*l* ( )	*r*	*i*
Derivatives of d-camphoric acid·					
Camphoric acid salts (*W*), esters (*f*)		+			
Camphoryl chloride, $C_{10}H_{14}O_2Cl_2$	*f*				
diamide, imide	*C*				
Camphoryl anhydride, $C_{10}H_{14}O_3$	*B*, *C*				*i*
Isocamphoric acid, $C_{10}H_{16}O_4$	*A*	*l* (+)	*d* (−)		
Esters of the *l*-acid	*f*		−		
Isocamphoric acid, anhydride	*B*				*i*
Camphocarboxylic acid, $C_{10}H_{15}O\ COOH = C_{11}H_{16}O_3$	*A*	*d* (+)	*l* ( )		
Camphocarboxylic acid esters and methylcamphocarboxylic acid esters	*f*	*d* (+)			
Oxycamphocarboxylic acid, $C_{11}H_{18}O_4$, and esters	*A*	*d* (+)			
Cyancampholic acid, $C_{10}H_{17}O_2.CN$, and oxycamphocarbaminic acid	*A*	*d* (+)			
Camphoronic acid, $C_9H_{14}O_6$	*W*	*d* (+)	*l* ( )	*r*	
Fenchone, $C_{10}H_{16}O$	*A*	+		*r*	
Fenchyl alcohol (fenchol), $C_{10}H_{17}OH$	*A*	*l* (+)	*d* ( )		
Fenchone oxime, $C_{10}H_{16}NOH$.	*A*	*d* (+)	*l* ( )		
Derivatives of fenchone oxime·					
Fenchone nitrile, $C_{10}H_{15}N$	*A*	*d* (+)			
Fenchylamine, $C_{10}H_{17}NH_2$	*A*	*l* (+)	*d* ( )		
Benzylidene fenchylamine	*A*	*l* (+)	*d* ( )		
Formyl, acetyl, propionyl, butyryl fenchylamine	*C*		*d* ( )		
o- and *p*-Oxy- and methoxybenzylidene fenchylamine	*C*	*d* (+)			
Pulegone, $C_{10}H_{16}O$	*f*	+			
Pulegone hydrobromide, $C_{10}H_{16}O\ HBr$	*A*		*d* ( )		
Pulegone oxime, $C_{10}H_{16}NOH$, and hydrochloride	*A*		*d* ( )		
Thujone, *Tanacetone*, $C_{10}H_{16}O$	*f*	+			
Carvol, $C_{10}H_{14}O$	*f*	+			*i*[1]
Hydrogen sulphide carvol, $C_{10}H_{14}O.H_2S$	*C*	*d* (+)	*l* ( )		
Dihydrocarveol, $C_{10}H_{18}O$	*f*	*d* (+)	*l* ( )	*r*	
Dihydrocarvone, $C_{10}H_{16}O$, *f*, and dihydrocarvoxime, $C_{10}H_{16}NOH$	(?)	*l* (+)	*d* ( )	*r*	
Eucarvol, $C_{10}H_{14}O$	*f*				*i*

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[1] Carvacrol.

Aliphatic Camphors and Terpenes.

Licareol (Aurantiol, lavendol, nerolol, linalool), $C_{10}H_{18}O$, $[(CH_2 = C.CH_3—CH_2—CH = CH)(H)C(CH_3)(CH_2.CH_2.OH)]$	*f*		—	
Coriandrol (*d* licareol) $C_{10}H_{18}O$	*f*	—		
Rhodinol (citronellol) $C_{10}H_{18}O$	*f*	—[1]	—[2]	r[3]
Citral, $C_{10}H_{16}O$	*f*			r
Ionone, $C_{13}H_{20}O$	*f*			i
Irone, $C_{13}H_{20}O$	*f*	—		
Citronellal, $C_{10}H_{18}O$	*f*	—		

29. *Ethereal Oils. Essential Oils.*

+		—		— and —	
Angelica	Oil	Asafoetida	Oil	Andropogon	Oil
Basil	"	Carrot	"	Cajeput	"
Bergamot	"	Copaiba	"	Cedarwood	"
Betel	"	Cubeb	"	Eucalyptus	"
Calamus	"	Curled mint	"	Fir needle	"
Caraway	"	Elemi	"	Sandalwood	"
Cardamom	"	Frankincense	"	Turpentine	"
Cascarilla	"	Geranium	"		
Celery	"	Ginger	"		
Chamomile	"	Gurjun balsam	"		
Chekenleaf	"	Hemlock	"		
Coriander	"	Hemp	"		
Costus	"	Juniper	"		
Dill	"	Kneepine	"		
Fennel	"	Lavender	"		
Lemon	"	Onion	"		
Lime	"	Parsley	"		
Mace	"	Rose	"		
Marjoram	"	Rue	"		
Mandarin	"	Silver fir	"		
Mastic	"	Storax	"		
Muscat	"	Tansy	"		
Myrtle	"	Thuja	"		
Orange	"	Thyme	"		
Orange blossom	"	Wormseed	"		
Para-coto bark	"	Ylang-ylang	"		
Pine needle	"				
Poley	"				
Savin	"				
Sassafras	"				
Spike	"				
Star anise	"				

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[1] From licareol acetate, mellisa oil or citronella oil.
From rose oil
[3] Geraniol.

30 *Resin Acids*				
Dextropimaric acid, $C_{20}H_{30}O_2$	*A*	+		
Podocarpic acid, $C_{17}H_{22}O_3$	*A*	+		
α- and β-Amyrin, $C_{30}H_{50}O$	*A*	+		
Sylvic acid, $C_{20}H_{30}O_2$	*A*		—	
Guaiacic acid, $C_{20}H_{26}O_4$	*A*		—	
Elemi acid, $C_{35}H_{56}O_4$	*A*		—	
Abietic acid, $C_{19}H_{28}O_2$	*A*		—	
31 *Aromatic Amines.*				
Diphenylethylenediamine (NH$_2$)(C_6H_5)(H) C—C(H)(C_6H_5)(NH$_2$)	*E*	+	—	*r*
α-Tetrahydronaphthylamine hydrochloride	*W*	+	—	*r*
1-5—Tetrahydronaphthylenediamine hydrochloride	*W*	+	—	*r*
32 *Alkaloids*				
a Alkaloids, of which Several Optical Modifications are Known, and Related Bodies				
α-Methylpiperidine (α-pipecoline), $C_5H_{10}NCH_3$	*f*	+	—	*r*
β-Methylpiperidine (β-pipecoline), $C_5H_{10}NCH_3$	*f*	+	—	*r*
α-Tetrahydroquinaldine, $C_{10}H_{13}N$		+	—	*r*
α-Ethylpiperidine, $C_5H_{10}NC_2H_5$	*f*	+	—	*r*
α-Propylpiperidine, α-conine, $C_5H_{10}NC_3H_7$ (natural conine, +)	*f*	+	—	*r*
Isoconine from + conine (?)	*f*	+		
Conhydrine (conydrine) and pseudoconhydrine, $C_8H_{17}NO$	*f*	+		
Coniceine, $C_8H_{15}N$(α- β- and γ forms inactive) *d*-form	*f*			
Coniceine, $C_8H_{15}N$ ε-form	*f*	+		
Paraconine, $C_8H_{17}N$ (isopropylpiperidine)	*f*			
α-Isobutyl-piperidine, $C_5H_{10}NC_4H_9$	*f*			
Ecgonine, $C_9H_{15}NO_3$, hydrochloride	*W*	|		
Esters of ecgonine A +	*W*	*d* (+)	*l* ( )	
Cinnamyl-ecgonine methyl ester (C_6H_7 $C_9H_{14}O$ CH_3 NO_3), hydrochloride	*W*	*d* (|)	*l* ( )	
Benzoyl-ecgonine methyl ester (cocaine), $C_{17}H_{21}NO_4$	*C*	*d* (|)	*l* ( )	
Anhydro-ecgonine, $C_9H_{13}NO_2$ from + and — ecgonine	*W*	*d* ( )	*l* ( )	
Ecgoninic acid, $C_7H_{11}NO_3$, from + and — ecgonine	*W*	*d* ( )	*l* ( )	
Tropinic acid, $C_8H_{13}NO_4$, from + and — ecgonine	*W*	*d* (|)	*l* (|)	
Atropine, $C_{17}H_{23}NO_3$	*A*	|		
Hyoscyamine, $C_{17}H_{23}NO_3$	*A*			

Pseudohyoscyamine, $C_{17}H_{23}NO_3$	*A*		—	
Hyoscine, $C_{17}H_{21}NO_4$	*A*		—	
Tropine, $C_8H_{15}NO_3$	*A*			*i*

b Alkaloids, of which Only One Optical Modification is Known

Nicotine, $C_{10}H_{14}N_2$	*f*		—
Salts	*W*	+	

Solid Alkaloids

The direction of rotation is given for the free bases, dissolved in alcohol or chloroform, and for the salts dissolved in water. Alkaloids which have been found to be inactive are also included.

Alkaloids of Cinchona Bark

	Base	Salt
Paricine, $C_{16}H_{18}N_2O$	*i*	
Cinchotenine, $C_{18}H_{20}N_2O_3$	+	+
Cinchotenicine, “	+	+
Cinchotenidine, “	—	—
Cinchonine, $C_{19}H_{22}N_2O$	+	+
β-and δ-Cinchonine, “	+	
Benzoylcinchonine, “	—	
α-Isocinchonine, Cinchoniline, “	+	+
β-Isocinchonine, Cinchonigine, “	+	+
Apocinchonine, “	+	+
Diapocinchonine, “	+	+
Isoapocinchonine, “	+	
Apoisocinchonine, “	+	
Homocinchonine, “	+	+
Pseudocinchonine, “	+	+
Cinchonifine, “	+	
Cinchonicine, “	+	+
Dicinchonine, “	+	+
Cinchonidine “	—	—
β- and γ-Cinchonidine, “	—	—
Apocinchonidine, “	—	—
Homocinchonidine, “	—	—
Apoquinamine, “	*i*	—
Cincholeuponic acid, $C_8H_{13}NO_4$	+	+
α- and β-Oxycinchonine, $C_{19}H_{22}N_2O_2$	+	+
Apoquinidine, “	+	+
Apoquinine, “	—	—

	Base	Salt
Cupreine, $C_{19}H_{22}N_2O_2$	—	—
Chitenine, $C_{19}H_{22}N_2O_4$	—	
Cinchonamine, $C_{19}H_{24}N_2O$	—	—
Cinchotine, “	—	
Hydrocinchonidine, “	—	—
Quinamine, $C_{19}H_{24}N_2O_2$	+	+
Conquinamine, “	—	+
Quinamicine, “	—	+
Quinamidine, “	—	*i*
Geissospermine, “	—	—
Quinidine, $C_{20}H_{24}N_2O_2$	—	—
Quinicine, “	—	—
Quinine, “	—	—
Acetyl-and propionylquinine	—	
Nitrocamphorquinine	—	
Hydroconquinine, $C_{20}H_{26}N_2O_2$	—	
Hydroquinicine, “		—
Hydroquinine, “	—	—
Chairamine, $C_{22}H_{26}N_2O_4$	—	
Conchairamine, “	—	
Chairamidine, “	—	
Conchairamidine, “	—	
Cusconine, $C_{23}H_{26}N_2O_4$	—	—
Concusconine, “	+	+
Aricine, “	—	*i*

Alkaloids of Opium

Morphine, $C_{17}H_{19}NO_3$	—	—	Laudanosine, $C_{21}H_{27}NO_4$	+
Codeine, $C_{18}H_{21}NO_3$	—	—	Laudanine, $C_{20}H_{25}NO_4$	
Methocodeine, $C_{19}H_{23}NO_3$	—		Cryptopine, $C_{21}H_{23}NO_5$	
Pseudomorphine, $C_{34}H_{36}N_2O_6$	—	—	Papaverine, $C_{20}H_{21}NO_4$	
Thebaine, $C_{19}H_{21}NO_3$	—	—	Narceine, $C_{23}H_{27}NO_8$	
Narcotine, $C_{22}H_{23}NO_7$	—	+	Pseudonarceine, $C_{23}H_{27}NO_8$	

Alkaloids of Strychnos Species.

Strychnine, $C_{21}H_{22}N_2O_2$	—	—	Brucine, $C_{23}H_{26}N_2O_4$	—
Chlorstrychnine, $C_{21}H_{21}ClN_2O_2$	—	—		

Other Alkaloids.

Aconine, $C_{26}H_{41}NO_{11}$	+	—	Echitamine (Ditaine), $C_{22}H_{28}N_2O_4$	–
Aconitine, $C_{33}H_{45}NO_{12}$	+	—	Hydrastine, $C_{21}H_{21}NO_6$	–
Isoaconitine, napelline, $C_{33}H_{45}NO_{12}$	+	—	Imperialine, $C_{35}H_{60}NO_4$(?)	–
Lycaconitine, $C_{27}H_{34}N_2O_6$	+		Hydronicotine, $C_{10}H_{16}N_2$	–
Arginine, $C_6H_{14}N_4O_2$		+	Paytine, $C_{21}H_{24}N_2O$	–
Bulbocapnine, $C_{34}H_{36}N_2O_7$ (?)	+		Sparteine, $C_{15}H_{26}N_2$	–
Corydaline, $C_{22}H_{27}NO_4$	+		Aribine, $C_{23}H_{20}N_4$	
Oxyacanthine, $C_{18}H_{19}NO_3$	+	+	Berberine, $C_{20}H_{17}NO_4$	
Pelletierine, $C_8H_{13}NO$	+		Chelerythrine, $C_{17}H_{15}NO_4$	
Pilocarpine, $C_{23}H_{34}N_4O_4$	+		Cevadine, $C_{32}H_{49}NO_9$	
Quebrachine, $C_{21}H_{26}N_2O_3$	+		Delphinine, $C_{22}H_{35}NO_6$	
Hyoscyamine, $C_{17}H_{23}NO_3$	—	—	Delphinoidine, $C_{42}H_{68}N_2O_7$	
Pseudohyoscyamine, $C_{17}H_{23}NO_3$	—	—	Hydrastinine, $C_{11}H_{11}NO_2$	
Hyoscine, $C_{17}H_{21}NO_4$	—	—	Methylhydrastine, $C_{22}H_{23}NO_6$	
Aspidospermine, $C_{22}H_{30}N_2O_2$	—	—	Piperine, $C_{17}H_{19}NO_3$	
Aspidospermatine, $C_{22}H_{28}N_2O_2$	—		Staphisagrine, $C_{22}H_{33}NO_5$	
Colchicine, $C_{22}H_{25}NO_6$	—		Cytisine (Sophorine), $C_{11}H_{11}N_2O$	

33 *Glucosides.*

Apiin, $C_{27}H_{32}O_{16}$	*A*	+	Helicin, $C_{13}H_{16}O_7$
α- and β-Chinovin, $C_{30}H_{48}O_8$ (?)	*A*	+	Hesperidin, $C_{22}H_{26}O_{12}$
Coriamyrtin, $C_{30}H_{36}O_{10}$	*A*	+	Naringin (Aurantiin), $C_{21}H_{26}O_{11}$
Amygdalin, $C_{20}H_{27}NO_{11}$	*W*	—	Phloridzin, $C_{21}H_{24}O_{10}$
Coniferin, $C_{16}H_{22}O_8$	*W*	—	Populin, $C_{20}H_{22}O_8$
Glycovanillin, $C_{14}H_{18}O_8$	*W*	—	Salicin, $C_{13}H_{18}O_7$
Convallamarin, $C_{23}H_{44}O_{12}$	*A*	—	Tetrabutyrylsaponin, $C_{19}H_{26}O_{10}(C_4H_7O)_4$
Glucoside from ivy leaves, $C_{32}H_{54}O_{11}$	*A*	—	Thevetin, $C_{54}H_{84}O_{24}$

The synthetic glucosides and analogous compounds with other s are given under the latter head.

34. *Bitter Principles (Santonin Group), Coloring-Matters and Unclassified Compounds.*

Santonin Group

Santonin, $C_{15}H_{18}O_3$	*C, A*	−	Santonyl bromide, $C_{15}H_{19}O_3Br$...........	*C*	−
α- and β-Metasantonin, $C_{15}H_{18}O_3$..............	*A*	+	Santonyl iodide, $C_{15}H_{19}O_3I$	*C*	−
Santonide, $C_{15}H_{18}O_3$...	*C, A*	+	Parasantonic acid (and esters), $C_{15}H_{20}O_4$........	*C*	−
Parasantonide, $C_{15}H_{18}O_3$. .	*C*	+	Metasantonic acid, $C_{15}H_{20}O_4$	*C*	−
Metasantonide, $C_{15}H_{18}O_3$ ..	*C*	−	Dehydrophotosantonic acid, $C_{15}H_{20}O_4$.........	*A*	+
Santonous acid (and esters), $C_{15}H_{20}O_3$...	*A*	+	Photosantonic acid, $C_{15}H_{22}O_5$............	*A, C*	−
Isosantonous acid (and esters), $C_{15}H_{20}O_3$, ...	*A*	*i*	α-Ethylphotosantonate ...	*A*	−
Disantonous acid ($C_{15}H_{19}O_3$)$_2$...........	*A*	+ − *r*	β- " " "	*A*	+
Santoninic acid (and salts) $C_{15}H_{20}O_4$	*A*	−	Isophotosantonic acid, $C_{15}H_{22}O_5$........	*A*	+
Santonic acid (and esters), $C_{15}H_{20}O_4$..	*C*	−	Hydrosantonic acid, $C_{15}H_{22}O_4$..............	*A*	+
Santonyl chloride, $C_{15}H_{19}O_3Cl$..	*C*	+			

Other Bodies.

Echicerin, $C_{30}H_{48}O_2$.. .	*C, E*	+	Quassiin, $C_{32}H_{42}O_{10}$(?) . .	*C*	+
Echitin, $C_{32}H_{52}O_2$....	*C, E*	+	Asebotoxin, $C_{31}H_{51}O_{10}$(?).	*C*	+
Echitein, $C_{42}H_{70}O_2$	*C, E*	+	" "	*W, A*	−
Echiretin, $C_{35}H_{56}O_2$	*E*	+	Picrotoxin, $C_{12}H_{14}O_5$.....	*A*	−
Euphorbon, $C_{15}H_{24}O$	*C*	+	Erythrocentaurin, $C_{27}H_{24}O_8$	*A*	*i*
Lactucerin, $C_{28}H_{44}O_2$ (?) ..	*E*	+	Ostruthin ($C_{14}H_{17}O_2$)$_n$.	*A*	*i*
Lactucol, $C_{13}H_{20}O$. .	*E*	+	Hematoxylin, $C_{16}H_{14}O_6$.	*A*	+

35 *Bile Acids.*

Cholanic acid, $C_{20}H_{28}O_6$ ...	*A*	+	α- and β-Hyoglycocholic acid, $C_{26}H_{43}NO_5$, Na salt......	*A*	+
Cholalic acid (and salts and esters), $C_{24}H_{40}O_5$..	*A*	+	α- and β-Hyoglycocholic acid, $C_{26}H_{43}NO_5$, Na salt......	*W*	*i*
Desoxycholic acid		+	Taurocholic acid, $C_{26}H_{45}NSO_7$ and Na salt.	*W*	+
Isocholanic acid, $C_{25}H_{38}O_7$...	*A*	−	Lithobilic acid, $C_{30}H_{58}O_6$ ...	*A*	+
Dehydrocholic acid, $C_{25}H_{36}O_5$	*A*	+			
Bilianic acid, $C_{25}H_{36}O_8$	*A*	+			
Glycocholic acid, $C_{26}H_{43}NO_6$ and Na salt	*A*	+			

36. *Proteid Substances.*

Egg albumin	*W*	—	Syntonin	*W* + HCl
Serum albumin	*W*	—	Propeptone	*W*
Casein,	*W* (+ HCl or NaOH)	—	Protalbumose	*W*
Serum globulin	NaCl sol	—	Deuteroalbumose	*W*
Lactalbumin	*W*	—	Heteroalbumose	*W* + NaCl
Glutin	*W*	—	Fibrin peptone	*W*
Chondrin	*W* + NaOH	—	Elastin peptone	*W*
Hemielastin	*W*	—	Vegetable peptone	*W*
Paralbumin	*W* + NaOH	—	Fibrinógen	*W* + NaCl
Mycoprotein	*W* + NaOH	—		

37. *Derivatives of Asymmetric Nitrogen.*

Methylethylpropylisobutylammonium chloride, $N(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)Cl$	*W*	
Compounds of the chloride with $PtCl_4$ and $AuCl_3$	*W*	
Acetic acid salt of the base	*W*	
Sulphuric acid salt of the base	*W*	
α-Benzylphenylallylmethyl-*d*-camphor sulphonate, $C_6H_5 CH_2.N(C_6H_5)(C_3H_5)CH_3.SO_3C_{10}H_{15}O$	*W*	+
Iodide, $C_6H_5 CH_2—N(C_6H_5)(C_3H_5)(CH_3)I$	acetone + acetic ether	+
Bromide, $C_6H_5.CH_2—N(C_6H_5)(C_3H_5)(CH_3)Br$	*A*	+

38 *Derivatives of Asymmetric Sulphur.*

d-Methylethylthetine *d*-camphor sulphonate	*W*	+
d-Methylethylthetine *d*-brom camphor sulphonate	*W*	+
d-Methylethylthetine platinichloride	*W*	+

As the table shows, a great many active bodies are knov and mainly from the animal or vegetable organism, wh have been found only in the one form, either right or l rotating. On the other hand, of the synthetically prepa active bodies, the constitution of which has been establish the greater number are already known in the two active mo fications, and also in the racemic form An enumeration the substances given in the tables shows this result:

Right rotating only	286	625
Left rotating only	237	
Right and left rotating	102	
Racemic forms		73

If the salts and esters of the active acids and bases, wh were not included, be counted in, the number of active bodies known at the present time [1898] will be over 700. At the time of the appearance of the first edition of this book, 1879, the number was about 300.[1]

On the relation of crystalline form to direction of rotation of bodies of these groups consult § 12.

III. NATURE OF THE ROTATING POWER

9. Distinction between Crystal Rotation and Liquid Rotation—Rotation of Vapors—Molecular Rotation.—The fact that bodies of the first class exhibit rotating power in the crystalline condition only, and lose this power completely when brought into solution, shows that the cause of the rotation must depend on the crystalline structure; that is, on a definite arrangement of molecular groups (crystal molecules). In fusing or dissolving the body, this is destroyed, and the optical activity disappears. The phenomenon is here, therefore, a purely physical one.

Substances of the second and third classes, on the contrary, rotate in the liquid condition It is probably true of bodies in this condition that the smallest amount of substance acting as a unit, does not consist in single chemical molecules, but in molecular aggregations. There are grounds for believing that, at least in concentrated solutions of a solid body in a liquid, the solid is not completely separated into single molecules or further into its ions, but that molecular groups or aggregations exist If then, a liquid is found to possess rotating power it is conceivable that the origin of this, as in the case of crystals, should be found in a definite structure of these molecular groups. In this event, the phenomenon would fall in the field of physics.

If the cause just suggested is sufficient, it follows that the rotating power of an active substance must disappear as soon as the same is decomposed into single molecules ; that is, as soon as it is brought into the condition of a true vapor. This important experiment was undertaken first by Biot[2] in the year 1817. He allowed turpentine vapor to pass through a metallic tube

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[1] Since the above was written nearly 100 new active compounds, mainly esters and complex substitution products, have been added to the list. Tr. (1900).

[2] Biot: Mem. de l'Acad., 2, 114.

30 meters in length, and closed at both ends with glass pla and observed that it possessed the power to produce rotatioı the polarized ray Exact measurements could not be mad the vapor suddenly became inflamed and destroyed apparatus. It was not until 1864 that the experiment repeated, and by Gernez,[1] who, by the aid of excellent ins ments, determined the rotation of a number of active liq with increasing temperature and finally in the state of va The substances tested were sweet orange oil (+), bi orange oil (+), turpentine oil (—), and camphor (+) all cases the specific rotation, [α] (that is the rotation culated for unit density and unit length of active lay decreased with increase of temperature, and finally when vapor was examined it was found that the specific rotation decreased to an extent, corresponding to the increas temperature. In illustration of this, the following num obtained from oil of turpentine and camphor are given

State of aggregation	Temperature	Density referred to water d	Observed angle of rotation a	Length of the observation tubes in decimeters l	S ro
		Turpentine oil (left rotating)			
Liquid	11°	0 8712	15 97°	0 5018	
	98°	0 7996	14 47°	0 50215	
	154°	0 7505	13 50°	0.50237	
Vapor	168°	0 003987	5 76°	40 61	

Observed vapor density at 168° = 4 981
Theoretical vapor density = 4 700.

State of aggregation	Temperature	Density referred to water d	Observed angle of rotation a	Length of the observation tubes in decimeters l	S ro
		Camphor (right rotating)			
Fused	204°	0 812	31 46°	0 5509	
Vapor	220°	0.003843	10.98°	40 63	

Observed vapor density at 220° = 5 369.
Theoretical vapor density = 5.252

The density of the vapor at the temperature of the ex ments, is, as is readily seen, very nearly the same as the t retical density, and it follows from this that single molec mainly, and not molecular aggregations, must have acte the polarized ray.[2] As, moreover, the specific rot

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[1] Gernez Ann scient. de l'École norm sup, I, I

[2] Ph A Guye and P. do Amaral have recently observed (Arch sc ph Genève [3], 33, 409, 513, Wied Beibl. 1895, 792, 894) agreement in the specific r

remains undiminished, the optical activity must be a property inherent in the molecule and must have its origin in the arrangement of the atoms in the same. The phenomenon, therefore, belongs in the domain of chemistry.

The optical activity of crystals on the one hand, and of liquids on the other, are, accordingly, two quite distinct phenomena, and to indicate that the latter resides in the individual molecule, Biot gave to it the name *molecular rotation*.

But this term has already been applied, as mentioned in § 3, to the product of the specific rotation by the molecular weight; that is, the quantity $[M] = \frac{M}{100}[\alpha]$ To avoid confusion it may be better in the latter case to use with the term, molecular rotation, the symbol [M]

10. **The Optical Theory of Circular Polarization in Quartz** was first enunciated by Fresnel.[1] This theory assumes that parallel to the principal axis in quartz a peculiar kind of double refraction takes place, and of such a character that a linearly polarized entering ray is decomposed into two rays which move forward in helical paths, one being inclined toward the left and the other toward the right On leaving the crystal these circularly polarized rays unite to form again a linearly polarized ray, but if they had moved through the crystal medium with unequal velocities, it would follow that the new plane of oscillation would be different from that of the entering ray It would be turned in the clock-hand direction, that is, to the right, when the polarized ray deviated in the same direction moved with a greater velocity than the other, and *vice versa* The existence of these two rays in quartz was first shown experimentally by Fresnel, and later by Stefan,[2] and also by Dove,[3] who found that they are absorbed by colored quartz (amethyst) in unequal proportions. The theory of

of a number of amyl derivatives in the liquid and vapor condition. An exception noted that valeraldehyde as vapor, rotates only about half as much as it does as a liquid may be accounted for by the chemical change or racemization which takes place by change of temperature in this substance.

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[1] Fresnel: Ann chim. phys [1], 28, 147

[2] Stefan Pogg. Ann., 124, 623.

[3] Dove: Pogg. Ann., 110, 284.

circular polarization has received a very full mathematic treatment at the hands of many physicists, and for th reference must be made to other works.[1]

In regard to the structure, which a crystalline medium mu have in order that it may effect a rotation of the plane polarization, the theory assumes an uneven condensation the ether around the molecules of the body, and to such a extent that this can not be considered as infinitesimally sma as compared with the wave length of the transmitted ligh This naturally depends on a definite molecular structure of t substance. The connection of direction of rotation in acti crystals with the existence of right or left hemihedral plan has led to the hypothesis, that in these crystals the partic are arranged with reference to each other in the form of right- or left-handed screw (spiral stair form). This vie expressed by Pasteur,[2] Rammelsberg,[3] and others, has receiv a great degree of probability through an experiment first tri by Reusch,[4] and later followed up by Sohncke[5] If a numb of thin plates of optically biaxial mica (12 to 36) are so place one on top of the other, that the principal axis of each o makes always the same angle (45°, 60°, 90° or 120°) wit the preceding one, a column is produced which, like an acti crystal, has the power of rotating the plane of transmitte polarized light, and either to the right or left as opposed to t direction of the twist in the column of plates. The optic behavior of such mica combinations[6] has been thorough studied by Sohncke who found that by sufficiently diminishi the thickness of the mica plates, a combination is secure the rotating power of which follows exactly the laws that ho for active crystals, that is, the amount of rotation is pr portional to the length of the column, and nearly proportion inversely to the square of the wave length.[7] Based on a theor of crystal structure developed by himself, Sohncke has furth shown[1] that not only in the trapezohedral-tetartohedral group of the hexagonal system, but also in others of the hexagonal and of the tetragonal and regular systems, a certain spiral-stair arrangement of the crystal particles can exist which is accompanied by rotation of the plane of polarization (See § 5). By means of mica plates of different thicknesses, arranged one upon the other with the axes inclined at different angles, it is possible to imitate the right- and left-handed forms of such active structures. A conception very similar to that of Sohncke, as to the cause of crystal rotation has been developed by Mallard;[2] Wyrouboff also assumes the building up of layers of biaxial plates.[3]

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[1] See Winkelmann "Handbuch d Physik," Breslau, 1894, Vol II, part 1, pa 784, Ketteler "Theoretische Optik," Braunschweig, 1885; Verdet "Leçons d'Optiq physique"

[2] Pasteur Consult § 12

[3] Rammelsberg Ber d. chem Ges, 2, 31

[4] Reusch Pogg. Ann, 138, 628

[5] Sohncke *Ibid*, Supplement, 8, 16.

[6] These columns may be obtained from Steeg and Reuter in Homburg.

[7] L Sohncke "Theory of Crystal Structure" Leipzig, 1879

11. **Optical Constitution of Active Liquid Substances.**—For a given thickness of layer, active liquids possess the same rotating power in all directions; they exhibit, therefore, the same behavior observed in active regular crystals The property of circular double refraction is inherent in the latter, and if the analogy with active liquids is complete, the same property should be expected in these also. This question was definitely decided, after Dove[4] in 1860 had made some unsuccessful experiments, by E. v. Fleischl[5] in 1884, and according to the method of Fresnel, who determined the double refraction of quartz in the direction of its principal axis by the aid of a combination of right- and left-rotating quartz prisms[6] The apparatus used by v. Fleischl consisted of a glass trough in the shape of a parallelopipedon, 543 mm long, and 20 mm. wide, open above, and divided by means of glass plates set diagonally into 20 hollow prisms, with refractive angles of 120°, and two end prisms with angles of 60°. Fig. 3 gives a shortened illustration of the arrangement. The 22 compartments were filled alternately with right- and left-rotating

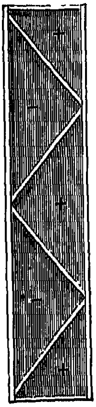

Fig 3

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[1] Ztschr. für Krystallog., 19, 529; 13, 214; 14, 426

[2] Traité de Cristallog, 2, 313 (1884).

[3] Wyrouboff · Ann. chim. phys [6], 8, 340; Jour de Physik [2], 5, 258 (1886); Bull Soc. Min., 13, 215 (1890).

[4] Dove · Pogg. Ann., 110, 290.

[5] E v. Fleischl Wiener Sitzungsber., 90, II, 478 (1884), also Wied Ann., 24, 127.

[6] See the text-books of physics.

substances, which, by proper dilution had been brought to possess exactly the same refractive indices. In a first series of experiments, solutions of saccharose and levulose were used, and in a second series, right orange-peel oil and left turpentine oil. When now a ray of light from a very fine opening (pin-hole) was passed through this system of prisms and examined by a reading telescope, two bright spots instead of one, were seen at the other end. If now the decomposition of the original light (ordinary or plane polarized) had followed as in the Fresnel experiment, the two emerging rays must be found circularly polarized, and in opposite directions. It was, in fact, shown by a well known method, employing a quarter wave length mica plate and rotating nicol, that the two rays had been transformed into two linear polarized rays with planes at right angles to each other. In two positions of the nicol, 90° apart, first one and then the other of the bright spots disappeared.

It is therefore apparent, through these experiments, that the optical cause of activity, that is to say, the manner of the wave motion of the ether, must be the same for liquids as for isotropic crystals. In all directions in both media, two waves are propagated, which are circularly polarized in opposite directions, and which move forward with unequal velocities. It has been mentioned that in such crystals this peculiarity is found, that they possess neither a plane of symmetry nor a center of symmetry, and further that they are found in enantiomorphic forms of which the one turns the plane of polarization to the right, and the other to the left. The same is to be assumed concerning active liquids, and as here the seat of the activity is found in the single molecules, it follows finally that an asymmetric structure must be assigned to the latter themselves.

This conception had been already reached in another way, and through the investigations of Pasteur carried out in 1848, which led to the following conclusions:

12. Investigations of Pasteur. Molecular Asymmetry.—As Biot and Seebeck[1] recognized in 1815, common tartaric acid rotates to the right, and in 1842 it was further observed by Mitscherlich[1] that racemic acid, isomeric with tartaric, is inactive. Pasteur[2] found next, that from a solution of racemic acid, rhombic-hemihedral crystals of a double salt having the composition, $NH_4NaC_4H_4O_6.4H_2O$, similar to the tartrate, could be obtained by slow concentration at a low temperature. But these crystals are not all identical in crystalline form, for two different structures may be easily recognized. Often the crystals appear developed as illustrated in Figs. 4 and 5, and in this case the differences may be easily recognized even by one not specially trained in crystallography[3] If the crystals are so placed that the two narrow surfaces, q and q^2, are turned toward the observer, it will be seen on some individuals that the small surface, o^1, is to the right of q and q^2 (Fig. 4), and on others, it will appear that this surface is to the left of q and q^2 (Fig. 5). There is exhibited here as in the case of quartz, the phenomenon of enantiomorphism, or "non-superposable hemihedry," as it was called by Pasteur; one crystal figure is the mirror image of the. other, and cannot be covered by it.

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[1] Biot and Seebeck Bull Soc Philom., 1815, 190

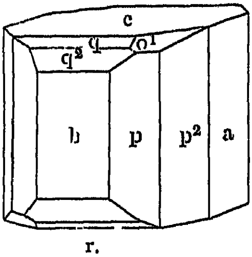

Fig 4

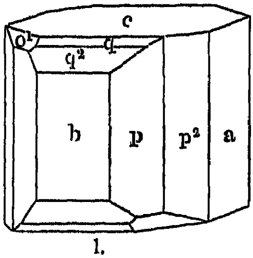

Fig 5

When Pasteur[4] had separated these two kinds of crystals mechanically, he found that those with the surface, o^1, to th right of q and q^2, when dissolved in water and examined in th polariscope, exhibited a right-hand rotation, while those wit o^1 to the left showed a left-hand rotation. From the tw crystallographically different sodium-ammonium salts h obtained, on the one hand, dextro-, and on the other, lev tartaric acid, and by mixing equal parts of these in aqueo solution he obtained an inactive liquid which, on evaporatio furnished crystals of racemic acid. Analogous relations we later found among many other active carbon compounds.

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[1] Mitscherlich Monatsber. der. Berl Akad., 1842.

[2] Pasteur: Ann. chim phys. [3], 24, 442; Compt. rend. 26, 535; 27, 367, 401, (1848); 29, 297 (1849); Ann chim. phys. [3] 28, 56 (1850), Compt rend. 31, 480 (1850); 32, 217, 549 (1851); Ann chim. phys. [3], 31, 67 (1851).

[3] Crystals with the same surfaces may appear also in forms, other than those shown, in such a case, measurements of angles are necessary to distinguish one kind from the other

[4] An explanation of the manner in which he was led to his discovery is given by Pasteur in his "Recherches sur la dissymétrie moléculaire des produits organiques naturels," Soc. chim. de Paris. Leçons de chimie professées in 1860. Paris 1861. See Alembic Club Reprint, No. 14.

In this way, it was for the first time shown that an acti substance may exist in two forms, right rotating and le rotating, the rotating power being under like conditions t same. From the observations, it was further apparent th the opposite asymmetric characteristics which the two kinds crystals of sodium-ammonium tartrate possess belong to the molecules also, inasmuch as after solution in water they sho right and left rotation. This led Pasteur to the view th the invidual molecules, as all other material objects, in respe to their forms and repetition of identical parts, fall natural into two classes. 1 Those which are superposable on the mirror images (as a straight-stair, a cube); 2 Those, who mirror images can not be covered by the originals and whi may appear in two oppositely constructed (enantiomorphi forms (spiral-stair, irregular tetrahedron, right and left scre right and left hand). Molecules of the first class possess symmetrical structure; in the second the atoms a asymmetrically ordered, and these should show optic activity. In relation to racemic acid, and the two tarta acids Pasteur[1] remarked. "Are the atoms of the right ac grouped in the form of a dextrogyrate helix, or do they sta at the corners of an irregular tetrahedron, or are they found a ranged in some other asymmetric form? We are not able to a swer these questions. But of this there can be no doubt. That a asymmetric arrangement of the atoms must exist in such manner as would furnish a non-superposable image It is ju as certain that the atoms of the left acid are arranged in manner exactly the reverse of those in the right, and final we know that racemic acid results from the combination of these two inversely asymmetric atomic groups"

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[1] "Recherches sur la dissymétrie moleculaire," Alembic Club Reprint, p 24.

Through these considerations, Pasteur introduced a new conception, that of *molecular asymmetry*, into the science. Before, however, this could bear fruit, a much wider development of organic chemistry was necessary, and only after the constitutional formulas of a large number of carbon compounds had been determined, was it found possible to trace a connection between the atomic structure of molecules and their optical activity.[1]

IV. RELATIONS BETWEEN ROTATING POWER AND CHEMICAL CONSTITUTION OF CARBON COMPOUNDS

13. Van 't Hoff-Le Bel Theory.—One of the most important advances in our knowledge of optical rotation was made in 1874, when J. H. van 't Hoff,[2] then in Utrecht, and a few weeks later J A LeBel,[3] in Paris, furnished the proof that optical activity has a definite connection with the structure of carbon compounds The fundamental conception founded on this notion, to which van 't Hoff was led through the assumption of a tetrahedral arrangement of the atoms, Le Bel, on the contrary, through Pasteur's idea of molecular dissymmetr found gradually decided confirmation through experimer and, as is well known, the later developments of the theor especially the views advanced by van 't Hoff on the arrang ment of the atoms in space, have created a new epoch in t science, that of stereochemistry.

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[1] An essentially different hypothesis to account for the activity of liquids as well as crystals, which is based on the assumption of the rotation of the molecules, has been proposed by Fock (Ber d chem Ges, **24**, 101) Wyrouboff (Ann chim phys [7], **1**, 5, Chem Centrbl, **1**, 260 (1894)) has sought to show that the rotation of crystalline organic substances in solution bears relation to the crystalline structure, and is not merely dependent on the nature of the chemical molecule

[2] First published in the paper Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuur-formules in de ruimte, benevens en daarmeê samenhangende opmerking omtrent het verband tusschen optisch actief vermogen en chemische constitutie van organische verbindingen, Utrecht, 1874 At the end the paper is signed September 5, 1874, J H van 't Hoff An abstract from this article appeared in 1875 in Bull Soc. Chim [2], **23**, 295 Then followed · 1 La chimie dans l'espace, par J. H. van 't Hoff, Rotterdam, 1875; 2. Die Lagerung der Atome im Raum, a German translation of the last by Dr F Hermann, Braunschweig 1877, 3. Dix années dans l'histoire d'une theorie, par J H van 't Hoff, Rotterdam 1887, 4. Stereochimie, by W Meyerhofer, a German edition, essentially of the Dix années, etc, Leipzig and Vienna, 1892, 5 Die Lagerung der Atome im Raum, von J. H. van 't Hoff, 2nd. ed., Braunschweig, 1894.

[3] Le Bel · First paper · Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolutions, Bull. Soc. Chim., [2] **22**, 337, November number, 1874. Then following papers: Bull. Soc. Chim. [2], **23**, 338 (1875), **25**, 546 (1876); **27**, 444 (1877); **33**, 106 (1880); **37**, 300 (1882); [3], **7**, 164; **8**, 613 (1892), Compt. rend, **89**, 312 (1879); **92**, 843 (1881); **110**, 144 (1890); **112**, 724 (1891); **114**, 304, 417 (1892).

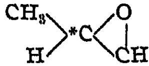
In this book we are concerned only with those portions the van 't Hoff-LeBel theory which are directly connect with optical activity, and these will be but briefly discussed they are found explained in all text-books of stereochemist and organic chemistry.

The fundamental points in the theory are as follows:

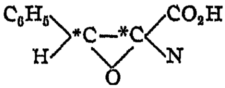
1. Consider in a compound of the type, CR_4, the carb atom situated in the center, and the four elements or grou joined to it situated at the corners of a tetrahedron, then case the four groups are all different, the resulting so formula $C(R_1R_2R_3R_4)$ will possess no plane of symmetry, a must exist in two non-superposable forms of which one is t mirror image of the other According to this view, everybo whose structural formula possesses a so-called asymmet carbon atom, that is, one which is combined with four diff ent atoms or groups, must be optically active and app in a right- and left-rotating form of equal rotating pow Experience has shown further that equal weights of t two modifications can unite to form an inactive compound mixture (racemic body) which by various means can be sp up into the active components

Asymmetric carbon atoms (*C) can appear in all dir methane derivatives, and chain structure molecules; in benze derivatives they can exist only in the side chains, but hydrated cyclic compounds also in the nucleus. Examp are found in the list of active substances given in § 8; a f other cases may be referred to here, from which it will be se that of the four radicals, two may be combined between the selves (propylene oxide), or one of the same with t different asymmetric carbon atoms (phenoxacrylic acid further, that the asymmetry of a carbon atom may depend remotely situated groups, and not necessarily on those imi diately connected (limonene, menthene)·

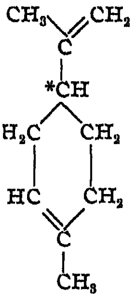
Propylene oxide



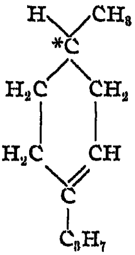
Phenoxacrylic acid



Limonene.



Menthene.



2. In substances which contain two asymmetric carbon atoms and whose molecules, like that of tartaric acid, $CO_2H—*CHOH—*CHOH—CO_2H$, are built up of two similar halves, there must be, according as these halves show the same or opposite rotations, besides the right- and left-rotating forms, a third inactive form depending on this intramolecular compensation, and which cannot be resolved into active components. Such an inactive form is not possible when the half molecules are dissimilarly constructed, but in this case, four active isomers may be expected, each two possessing equally strong, but oppositely directed rotations. If a compound contains several asymmetric carbon atoms, by addition or subtraction of the effects of the single groups, a large number of unequally strong active modifications may result, two of which again in each case belong together as antipodes, and finally the existence of some definite number of inactive compensation forms may also be expected

In all such cases, consideration will show how many of these optical isomers must exist when the structural formula of the substance is known. The method of making such a computation will be shown in the next chapter on Optical Modifications.

With the ethylene derivatives having four different radicals, $R_1R_2C{=}CR_3R_4$, the four groups must lie in one plane if we consider the carbon atoms united by an edge of the tetrahedrons containing them, and no asymmetry is possible. In fact, all ethylene derivatives have been found to be inactive,[1] even when made from active compounds, as for exam fumaric and maleic acids from malic acid, bromcinna acid, $C_6H_5—CBr=CHCO_2H$, from the dibrom $C_6H_5—CHBr—CHBr.CO_2H$, and others Likewise, no as metry is possible when in bodies of the type, $R_1R_2C=C$ an even number of doubly linked carbon atoms is introdu But, on the other hand, as van 't Hoff remarked,[1] asymm and optical activity appear if the number of added car atoms is uneven, inasmuch as the four radicals then st crossed, as is the case in the tetrahedron. The simp bodies of this kind would be the propadiene (allene) der tives; observations on such substances are wanting as yet.

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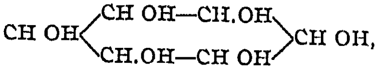
[1] Le Bel (Bull. Soc Chim. [3], 8, 613) had considered optical activity possible in unsaturated compounds, and Perkin (Jour. Chem. Soc., 53, 695) believed he found this in chlorfumaric and chlormaleic acids, $CO_2H—CCl{=}CH—CO_2H$. Walden, however, showed the error in these observations (Ber. d. chem. Ges., 26, 210).

As van 't Hoff pointed out,[2] cyclic compounds present tain definite conditions of asymmetry, and to begin with, have the derivatives of tri- and tetramethylene, but ac bodies belonging here are not yet known. But many s appear in the six member rings, that is in the di-, tri- hexa-hydrated benzene derivatives. Among the last mos



$$\mathrm{CH\ OH}\left\langle\begin{array}{l}\mathrm{CH\ OH—CH.OH}\\ \mathrm{CH.OH—CH\ OH}\end{array}\right\rangle\mathrm{CH\ OH},$$

offers an example in which the existence of asymme carbon is not apparent from the formula, and in which asymmetry and the mirror image form appear only when position of the H and OH above and below the plane of carbon ring, that is to say, the *cis* and *trans* isomerism, is tal into consideration; anything further concerning this belon in the field of stereochemistry. Benzene derivatives which not hydrides can hold asymmetric carbon atoms in the s chains.

Confirmation of the van 't Hoff-Le Bel theory has co gradually, and in many different ways. It has been fou that without exception, activity is connected with the pr ence of asymmetric carbon, and that in bodies in which thi lacking, rotating power is not found. For a number of bod of the last class, such as N-propyl alcohol, styrol, β-picoli and others, in which activity was claimed, it was found tl this assertion was an error. Through direct experiments, the appearance or disappearance of optical activity by formation or destruction of asymmetric carbon atoms was further shown. Le Bel first proved this by the conversion of active amyl iodide, $CH_3.HC^*.C_2H_5.CH_2I$, into inactive methyldiethyl methane, $CH_3.C.H.C_2H_5.C_2H_5$.[1] Then Just[2] obtained from the same amyl iodide, by action of zinc and hydrochloric acid inactive dimethylethyl methane, $(CH_3)_2.C_2H_5.C.H$, but by action of ethyl iodide and sodium he obtained active methylethylpropyl methane, $CH_3.C_2H_5.C_3H_7\ {}^*C.H$; also, by heating with sodium, active diamyl,

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[1] "Lagerung der Atome im Raum," 2nd. ed. (1894), pp. 68 to 76.

[2] *Loc cit*, p 83 to 94

[3] See Bouveault Bull Soc. Chim. [3], 11, 144 (1894).

$$C_2H_5.CH_3\ H.{}^*C—CH_2—CH_2.—{}^*C.H.CH_3.C_2H_5$$

Further, it was shown that for the existence of optical activity the nature of the four radicals combined with the asymmetric carbon atom is a matter of no consequence. It was formerly observed that the introduction of a halogen led often to a disappearance of activity; thus from left-rotating malic acid, inactive bromsuccinic acid (Kekulé),[3] from left-rotating mandelic acid, inactive phenylbromacetic acid, $C_6H_5\ {}^*CHBr.CO_2H$ (Easterfield),[4] and from *d*- and *l*-isopropylphenylglycolic acid, inactive isopropylphenylchloracetic acid, $(C_6H_4\ C_3H_7)(H){}^*C(Cl)(CO_2H)$, (Fileti),[5] were obtained As was later found, the cause of the inactivity of these products lay in the fact that racemic forms were produced by reason of the high reaction temperature. By keeping this as low as possible, these halogen bodies were obtained in rotating condition. This was shown particularly by Walden, who prepared an active chlorsuccinic acid from malic acid by action of phosphorus pentachloride with addition of chloroform, and later from sarcolactic acid, ethyl tartrate, and mandelic acid, a large number of chlorine and bromine derivatives, such as methyl chlorpropionate, ethyl brommalate, phenylchloracetic acid, and others which all possessed optical activity.[6] Finally, the

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[1] Le Bel Bull. Soc Chim [2], **25**, 546 (1876).

[2] Just: Ann. Chem (Liebig), **220**, 146 (1883).

[3] Kekulé · Ann. Chem. (Liebig), **130**, 25 (1864).

[4] Easterfield Jour Chem. Soc., **59**, 75 (1891).

[5] Fileti: Gazz Chim., **22**, II, 405; J. prakt Chem. [2], **46**, 562

[6] Walden: Ber d. chem. Ges., **26**, 214 (1893). See further Le Bel. Bull. Soc. Chim., **9**, 674 (1893) and Ber. d. chem Ges., **28**, 1923 (1895); also Walden: Ber. d. chem. Ges, **28**, 2766.

fact was fully explained why many bodies exist which cont
asymmetric carbon atoms, but are nevertheless inactive.
some cases it was shown that they are racemic forms, inasm
as they are resolvable into active compounds; in other ca
as mesotartaric acid, dulcitol, and mucic acid, they contain
similarly constituted halves, and the inactivity follows fı
the opposite rotating power of these. In a third grour
asymmetric substances it was found that they possess a v
weak rotating power, and in order to recognize this, eith
very long column must be taken, or, as in the case of manni
some indifferent substance (boric acid) must be added
increase it It appears therefore, that in all cases the vi
of van 't Hoff and Le Bel are found to agree with experiei
and that when apparently a contradiction was found (limonen
later investigations removed this The doctrine of as
metric carbon atoms may be looked upon as one of the l
established of chemical theories

14. **Asymmetric Nitrogen and Sulphur.**—Compounds of tı
nitrogen with radicals different from each other appear alw
to be inactive, attempts to split up the tartaric acid salt
ethylbenzylamine (Kraft),[2] benzyl hydroxylamine (Behr
and König),[3] methyl aniline, tetrahydroquinoline, and te
hydropyridine (Ladenburg),[4] have led to no result.

On the other hand, an active compound of pentaval
nitrogen, isobutylpropylmethylethylammonium chloride
been obtained The inactive salt directly obtained
split up by Le Bel[5] by aid of the fungus culture method,
a left-rotating chloride ($[\alpha]_D = -7°$ to 8°) was obtain
which was further converted into active chlorplatinate, ch
mercurate, and acetate The chloraurate, rotating very fee
to the left, became dextrorotatory after addition of hyd
chloric acid. The sulphate was found to be inactive.

More recently another active compound of pentaval
nitrogen has been produced. Wedekind[6] attempted to reso

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[1] von Baeyer Ber. d chem. Ges , **27**, 436, Tiemann and Semmler . *Ibid.*, **28**,

[2] Kraft. Ber d. chem. Ges , **23**, 2780 (1890).

[3] Behrend and König: Ann. Chem (Liebig), **263**, 184 (1891).

[4] Ladenburg Ber d chem. Ges., **26**, 864 (1893)

[5] Le Bel Compt rend., **112**, 724 (1891).

[6] Wedekind: Ber. d. chem. Ges , **32**, 517.

α-benzylphenylallylmethylammonium hydroxide by combination with tartaric and camphoric acids, but without success. Pope and Peachey, however, by using the much stronger dextrocamphor sulphonic acid, which they have applied in several other cases, succeeded in effecting a perfect resolution.[1]

They mixed the iodide of α-benzylphenylallylmethylammonium with the silver salt of dextrocamphor sulphonic acid in molecular proportion, and boiled in a mixture of acetone and ethyl acetate. After separating silver iodide by filtration, the liquid left deposited, on cooling, a crystalline mass of the dextro- and levo-benzylphenylallylmethylammonium dextrocamphor sulphonates This was crystallized from acetone, the less soluble dextro constituent being readily obtained in colorless plates melting at 170°, and giving $[\alpha]_D = +44.4^\circ$ For the *l*-salt separated from the mother-liquors in less pure form, the rotation $[\alpha]_D = -18.6^\circ$ was found. By double decomposition of the camphor sulphonates,

$$C_6H_5\,CH_2.N(C_6H_5)(C_3H_5)(CH_3).SO_3.C_{10}H_{15}O,$$

the authors obtained the *d*- and *l*-iodides and bromides,

$$C_6H_5\,CH_2\,N(C_6H_5)(C_3H_5)(CH_3)I,\text{ or Br}$$

In recent years many attempts have been made to resolve asymmetric racemic sulphur compounds, but for a time without success See for example the work of Aschan.[2]

Very lately, however, and just as this translation is going to the press, Pope and Peachey[3] have applied their camphor sulphonic acid process to the resolution of methylethylthetine and have succeeded in separating an active body with the sulphur as the asymmetric element. The authors conclude from their work that a large number of other elements may be found to behave as asymmetric centers of optical activity Some details of their process will be given in a following chapter.

Ammonium derivatives containing two similar radicals as the chlorides of dimethylethylpropyl-, methylethyldipropyl-, ethyldipropylisobutyl-, and ethylpropyldiisobutylammonium cannot be converted, as Le Bel[1] found, into active for the action of fungi

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[1] Pope and Peachey J. Chem. Soc., 75, 1127.

[2] Aschan : Ber. d. chem. Ges., 32, 988.

[3] Pope and Peachey . J Chem. Soc., 77, 1072.

Further consideration of the subject of asymmetric nit belongs in the field of stereochemistry.

V. OPTICAL MODIFICATIONS

15. The fact that a body can exist in a right rotating, rotating, and an inactive form was first recognize mentioned, by Pasteur in 1848, in the case of tartaric The number of bodies acting similarly was increased slowly, and in 1879, at the time of the publication of the edition of this book, only three other examples could be g *viz.*, malic acid, camphor, and camphoric acid.

Already in 1875, van 't Hoff, in his "Chimie dans l'esp had developed the general formulas by which the numb possible stereoisomers and hence, also, optical isomers body could be calculated from the number of asymm carbon atoms in its molecule. For a long time the observa available, from which these formulas could be tested, entirely too scanty, and only in the last few years, the investigations of E Fischer, on the members of the s group, have furnished material which demonstrated pletely the correctness of the theoretical predictions. O vations were multiplied also, in other classes of compo and as the table of active substances given in § 8 shows, t are now over 100 such bodies known in different op modifications.

However, there is still a very large number of active bo over 300 in fact, which are known only in one form, s right, some left rotating. This is true of whole grou bodies as the polysaccharides, natural glucosides, st varieties, alkaloids, bitter principles, bile acids, and prot Without doubt, most of these contain several asymm carbon atoms, and must exist in different forms with diffe rotating powers as well as in inactive modifications.

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[1] Le Bel Compt rend, **112**, 724 (1891).

A. Calculation of the Number of Optical Modifications of a Compound from the Number of Asymmetric Carbon Atoms Contained in It.

16. If we divide the compounds consisting of a chain of singly linked carbon atoms into the three classes given below, the number of possible stereoisomers or optically active and inactive forms is shown in the following expressions in which .

n = the number of asymmetric carbon atoms in the compound.

N = the whole number of possible isomers, which are divided into

i = inactive, non-separable modifications, and

a = active forms, which occur in pairs as optical antipodes with equally strong opposite rotations These lead to

$r = \frac{a}{2}$ inactive separable racemic modifications

First class . n even or odd Structural formula not in two equal halves

If RR_1 represent the terminal radicals, and a, b, the radicals combined to the middle carbon atoms, the general type is

$$R—(^*Cab)_{1,\,2,\,3,} \quad —R_1$$

For example

Malic acids	...... $.CO_2H—^*CH.OH—CH_2—CO_2H$
Phenyl-α-chlorlactic acids	$.C_6H_5—^*CH\ OH—^*CHCl—CO_2H$
Pentoses	$CH_2OH—^*CH.OH—^*CH\ OH—^*CH\ OH—CHO$
Hexonic acids	... ...$CH_2OH—(^*CH\ OH)_4—CO_2H$

Bodies belong here in the chain of which there is at some point, a carbon atom which is not asymmetric (CH_2, CO_2, CO)

For example

Butylchloralaldol

$$CH_3—^*CHCl—CCl_2—^*CH.OH—^*CH(CHO)—^*CH\ OH—CH_3$$

In all such cases we have

$$\text{(I)}^1 \qquad N = 2^n \qquad a = 2 \qquad i = 0.$$

---

[1] The expressions (I) and (II) were first proposed by van 't Hoff ("La chimie dans e," 1875, p 9 and 12) and the second one is also found in this form

$$N = 2^{\frac{n}{2}} + \frac{2^n - 2^{\frac{n}{2}}}{2} \text{ or } 2^{\frac{n}{2}-1}\left(2^{\frac{n}{2}} + 1\right) \text{ or } \frac{1}{2}\left(2^n + 2^{\frac{n}{2}}\right)$$

Attention was first called to formula (III) by E Fischer (Ann Chem (Liebig), 270, 67 (1891)) These formulas are derived from the theorems on permutation and combinations, attention being paid to the conditions obtaining for various reversed and reflected image forms

Therefore:

$n =$	1	2	3	4	5	6
$N = a =$	2	4	8	16	32	64
$r =$	1	2	4	8	16	32

Second class. n even. Structural formula in two equal halves. The type is

$$R\text{—}(^*Cab)_{2,4,6,\cdot}\text{—}R$$

For example:

Tartaric acid.................. .....$CO_2H\text{—}^*CH\,OH\text{—}^*CH.OH\text{—}CO_2H$
Sym dimethylsuccinic acid ....$CO_2H\text{—}^*CH(CH_3)\text{—}^*CH(CH_3)\text{—}CO_2H$
Hydrobenzoin . ...$C_6H_5\text{—}^*CH\,OH\text{—}^*CH\,OH\text{—}C_6H_5$
Hexitols..... ....$CH_2OH\text{—}(^*CH\,OH)_4\text{—}CH_2\,OH$
Tetraoxydicarboxylic acid .....$CO_2H\text{—}(^*CH\,OH)_4\text{—}CO_2H$

Bodies are found here with symmetrically halved structural formulas which contain in the middle, an even number of non-asymmetric carbon atoms For example

Dimethyladipic acids, $CO_2H\text{-}^*CH(CH_3)\text{-}CH_2\text{-}CH_2\text{-}^*CH(CH_3)\text{-}CO_2H$
Diallylbromides, $CH_2Br\text{—}^*CHBr\text{—}CH_2\text{—}CH_2\text{—}^*CHBr\text{—}CH_2Br$

We have in the second class:

(II) $$N = 2^{n-1} + 2^{\frac{n}{2}-1}$$

$$a = 2^{n-1} \qquad i = 2^{\frac{n}{2}-1}$$

Therefore, when

$n =$	2	4	6	8
$N =$	3 ✓	10	36	136
$a =$	2	8	32	128
$i =$	1	2	4	8
$r =$	1	4	16	64

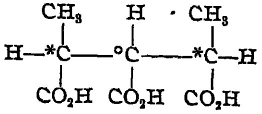
Third Class. n uneven. Structural formula equally halved, after excluding the middle carbon group. The type is

$$R\text{—}(^*Cab)_{3,5,7,\cdot\cdot}\text{—}R$$

Examples:

Trioxyglutaric acids, $CO_2H\text{—}^*CH\,OH\text{—}^\circ CH\,OH\text{—}^*CH\,OH\text{—}CO_2H$
α-Glucoheptitol, $CH_2\,OH\text{—}(^*CH\,OH)_2\text{—}^\circ CH\,OH\text{—}(^*CH\,OH)_2\text{-}CH_2\,OH$

Dimethyltricarballylic acid .....



$$\begin{array}{ccccc} & CH_3 & H & CH_3 & \\ H\text{—} & ^*C & \text{—}^\circ C\text{—} & ^*C & \text{—}H \\ & CO_2H & CO_2H & CO_2H & \end{array}$$

In these cases °C, the middle atom of the chain, is:

Asymmetric (active) when the other parts of the chain, the equal halves, are asymmetric similarly, that is, have the same direction of rotation;

Symmetric (inactive) when the two other parts of the chain are oppositely asymmetric, and therefore neutralize each other in their rotating power

Under both circumstances when the middle atom, °C. is included in the number n, we have the following formula for calculating the isomers:

$$\text{(III)} \qquad N = 2^{n-1}$$

$$a = 2^{n-1} - 2^{\frac{n-1}{2}} \qquad i = 2^{\frac{n-1}{2}}$$

From this it follows that for:

$n =$	3	5	7	9
$N =$	4	16	64	256
$a =$	2	12	56	240
i	2	4	8	16
r	1	6	28	120

In deriving the different stereoisomers of a body, it is convenient to employ the method of representation proposed by E. Fischer,[1] which consists in this, that the solid model of the molecule (built up by the aid of the well-known rubber carbon atom models) is placed in such a manner over the plane of the paper that all the carbon atoms are found in a straight line, and the radicals combined with them (H and OH), stand to the right and left above the plane. Then the projection of such a structure, for example, that of *d*-glucose is shown in the following diagram, I*a*, and that of *l*-glucose by the mirror image I*b*. A more contracted method of representation is shown in II and III, where, for the last case, H = • and OH = ×.

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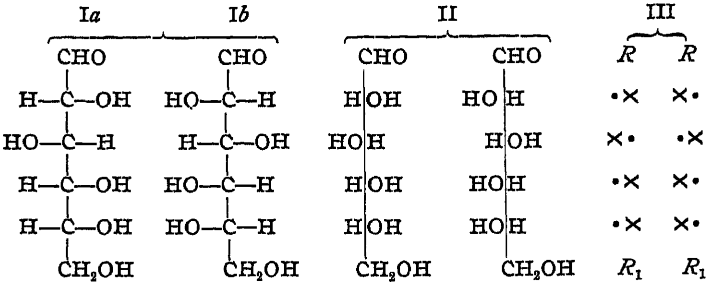
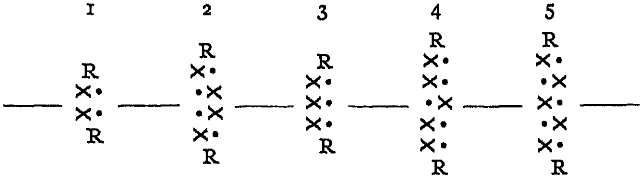
[1] Fischer. Ber. d. chem. Ges., 24, 2683.



The Inactive Non-Separable Modifications are distinguished in the following configuration formulas by this, that the latter may always be cut by a horizontal line into two equal halves of which the lower one is the mirror image of the upper. The compensation existing within the molecule is illustrated by this, for if in Diagram I, below, a spiral be drawn through the four radicals in the direction, $\overset{1}{\cdot}\ \overset{2}{\times}\ \overset{3}{R}\ (\ \cdot\ \overset{4}{\times}\ R)$, in the upper half of the figure it will be turned to the right, and in the lower to the left. In compounds which have in the chain an uneven number of carbon atoms, the cut passes through the middle (not asymmetric) one Such inactive molecules may be represented by the following diagrams:



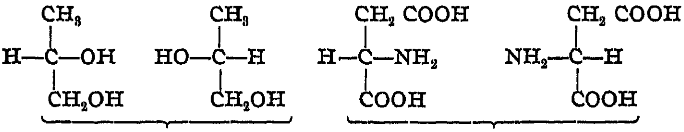
In what follows the derivation of the possible optical modifications for chain structure molecules with $n = 1, 2, 3, 4, 5$ will be carried through and illustrated.

I. $n = 1$.

First Class:

$$N = a = 2 \qquad i = 0 \qquad r = 1$$

For example.



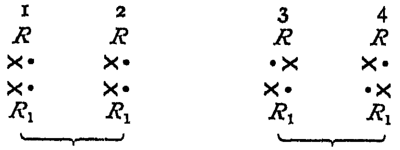
Right and left propyleneglycol   Right and left aspartic acid.

II. $n = 2$.

A. *First Class:*

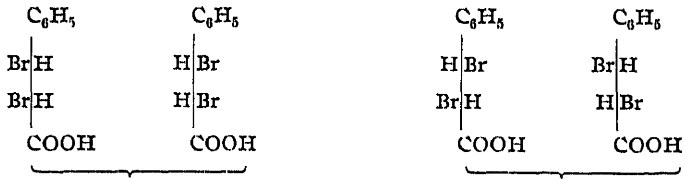
$$N = a = 4 \qquad i = 0 \qquad r = 2$$

The four possible active combinations, of which each pair form antipodes, are:



$$\underbrace{\begin{array}{cc} 1 & 2\\ R & R\\ \times\bullet & \times\bullet\\ \times\bullet & \times\bullet\\ R_1 & R_1\end{array}}\qquad\underbrace{\begin{array}{cc} 3 & 4\\ R & R\\ \bullet\times & \times\bullet\\ \times\bullet & \bullet\times\\ R_1 & R_1\end{array}}$$

An example of this is furnished by cinnamic acid dibromide of which the four active as well as the two racemic forms are known:



$$\underbrace{\begin{array}{r|l} \multicolumn{2}{c}{C_6H_5}\\ Br & H\\ Br & H\\ \multicolumn{2}{c}{COOH}\end{array}\qquad\begin{array}{r|l} \multicolumn{2}{c}{C_6H_5}\\ H & Br\\ H & Br\\ \multicolumn{2}{c}{COOH}\end{array}}\qquad\underbrace{\begin{array}{r|l} \multicolumn{2}{c}{C_6H_5}\\ H & Br\\ Br & H\\ \multicolumn{2}{c}{COOH}\end{array}\qquad\begin{array}{r|l} \multicolumn{2}{c}{C_6H_5}\\ Br & H\\ H & Br\\ \multicolumn{2}{c}{COOH}\end{array}}$$

Which of these configurations belongs to each isomer has not been established

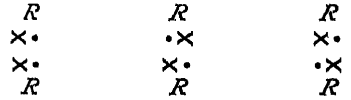
The same conditions must appear with:

Phenyl-α-chlorlactic acid . .	C_6H_5—CH OH—CHCl—CO_2H,
Phenyl-β-chlorlactic acid	C_6H_5—CHCl—CH OH—CO_2H,
Trioxybutyric acids	CH_2OH—CH OH—CH OH—CO_2H, etc.

B. *Second Class:*

$$N = 3 \qquad a = 2 \qquad i = 1 \qquad r = 1$$

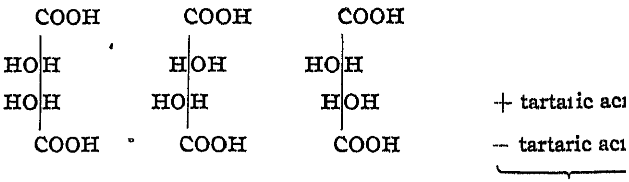
If $R = R_1$ of the four combinations given under A, 1 and 2 will be identical, as can be shown by rotating the diagram (turning it upside down), and there remain:



$$\begin{array}{ccc} R & R & R\\ \times\bullet & \bullet\times & \times\bullet\\ \times\bullet & \times\bullet & \bullet\times\\ R & R & R\end{array}$$

Inactive. Oppositely active.

Example ·



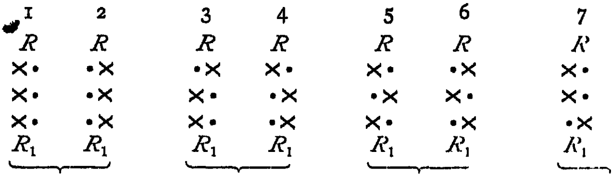
Meso- tartaric acid. Right tartaric acid. Left tartartic acid.

III. $n = 3$

A. *First Class:*

$$N = a = 8 \qquad i = 0 \qquad r = 4$$

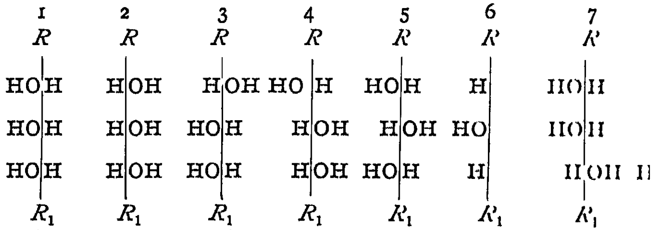
We have·



Example

$$\text{Pentoses} \ldots\ldots\ldots \overset{R_1}{CH_2OH}\text{—}(CH\,OH)_3\text{—}\overset{R}{CHO}$$

$$\text{Pentonic acids} \ldots\ldots\ldots CH_2OH\text{—}(CH\,OH)_3\text{—}COOH$$



l-Ribose *l*-Ribonic acid | Unknown | *l*-Arabinose. *l*-Arabonic acid | *d*-Arabinose | Unknown. | *l*-Xylose *l*-Xylonic acid | Lyxose Lyxonic acid | U

B *Third Class:*

$$N = 4 \qquad a = 2 \qquad i = 2 \qquad r \quad 1.$$

Of the configurations given under A the followin identical when $R = R_1$:

1 with 2 4 with 7
3 " 8 5 " 6

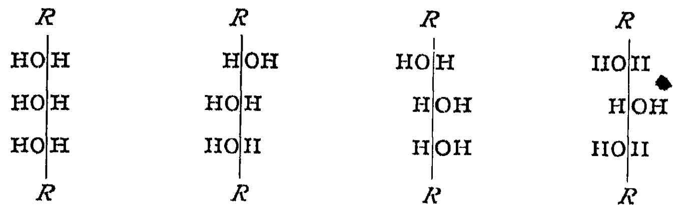
and there remain:

1	3	4	5
R	*R*	*R*	*R*
×•	•×	×•	×•
×•	×•	•×	•×
×•	×•	•×	×•
R	*R*	*R*	*R*
Inactive.	Oppositely active.		Inactive.

Example:

Pentitols . ...$CH_2OH—(CH.OH)_3—CH_2OH$

Trioxyglutaric acids..........$COOH—(CH.OH)_3—COOH$



Adonitol Ribotrioxy-glutaric acid Inactive

l-Arabitol. *l*-Trioxy-glutaric acid.

Unknown

Xylitol Xylotrioxy-glutaric acid. Inactive

IV $n = 4$.

A *First Class.*

$N = a = 16, \quad \iota = 0, \quad \iota \quad 8.$

1	2	3	4	5	6	7	8
R	*R*	*R*	*R*	*R*	*R*	*R*	*R*
×•	•×	•×	×•	×•	•×	×•	•×
×•	•×	×•	•×	•×	×•	×•	•×
×•	•×	×•	•×	×•	•×	•×	×•
×•	•×	×•	•×	×•	•×	×•	•×
R_1	R_1	R_1	R_1	R_1	R_1	R_1	R_1

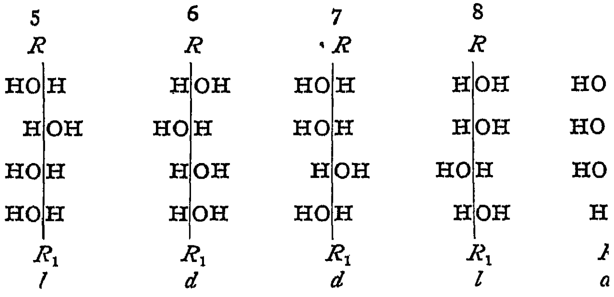
9	10	11	12	13	14	15	16
R	*R*	*R*	*R*	*R*	*R*	*R*	*R*
×•	•×	•×	×•	•×	×•	•×	×•
×•	•	•×	×•	×•	•×	×•	•×
×•	•×	×•	•×	•×	×•	×•	•×
•×	×•	×•	•×	×•	•×	•×	×•
R_1	R_1	R_1	R_1	R_1	R_1	R_1	R_1

Of these sixteen active configurations, in the

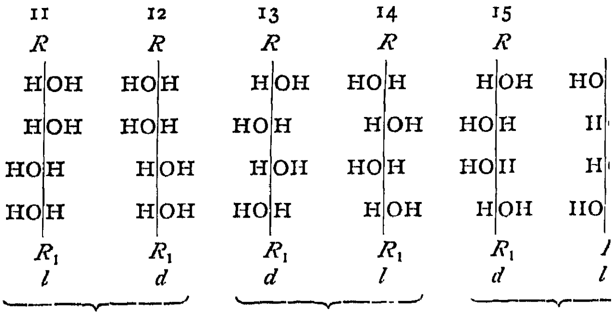
Hexoses .... $\overset{R_1}{CH_2OH}—(CH.OH)_4—\overset{R}{CHC}$

and Hexonic acids .. ..$CH_2OH—(CH\ OH)_4—COC$

the following are known.



Glucose, gluconic acid — Gulose, gulonic acid. — Talo talonic



Mannose, mannonic acid. — Idose, idonic acid. — Galactose, gal acid

B. *Second Class.*

$N = 10 \qquad a = 8 \qquad i = 2 \qquad i = 4$

This number of isomers follows from the configu given under A when R is taken equal to R_1, because the become identical:

1 with 2 — 5 with 8
3 " 10 — 6 " 7
4 " 9 — 15 " 16

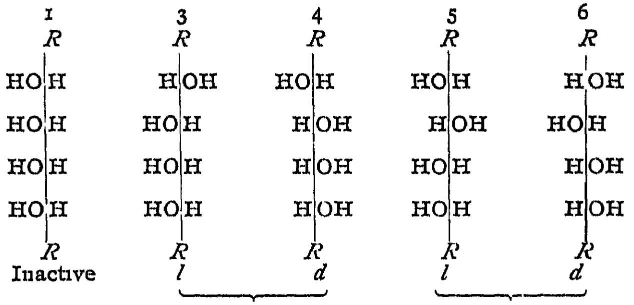
There remain then:

1 — (3, 4) — (5, 6) — (11, 12) — (13, 14) — 15.

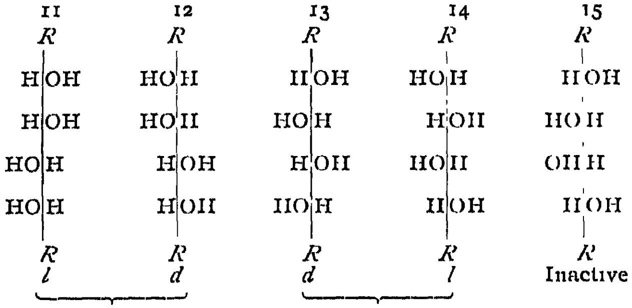
We have here

Hexitols . . . . $CH_2OH—(CH.OH)_4—CH_2OH$
and Saccharic acids . . . . $COOH—(CH.OH)_4—COOH$,

of the last of which the ten forms are known:



Allo-mucic acid. Talitol Talomucic acid. Sorbitol. Saccharic acid



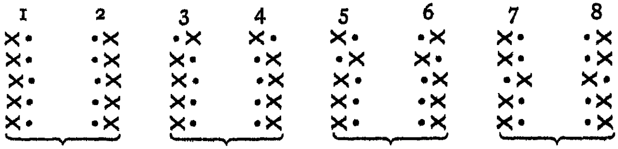
Mannitol Mannosaccharic acid. Iditol Idosaccharic acid. Dulcitol. Mucic acid

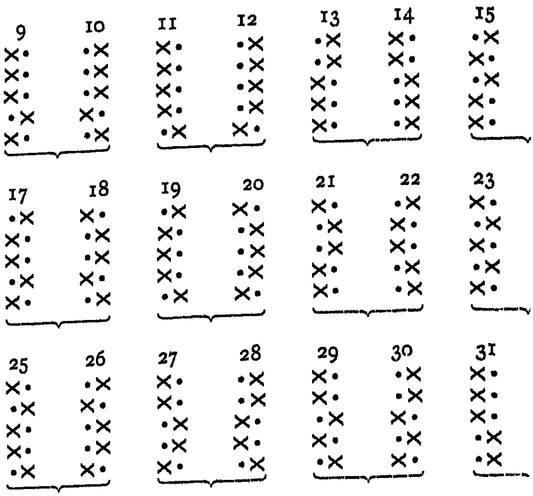
V $n = 5$.

A. *First Class*:

$N = a = 32 \qquad i = 0 \qquad r = 16$.

The thirty-two possible combinations are as follows, leaving out the symbols, R and R_1:

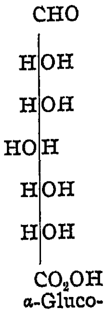




Of bodies belonging here, but few are known, c

ing to :

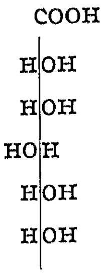
8



$$\begin{array}{r|l} \multicolumn{2}{c}{CHO} \\ H & OH \\ H & OH \\ HO & H \\ H & OH \\ H & OH \\ \multicolumn{2}{c}{CO_2OH} \end{array}$$

α-Gluco-
heptose.

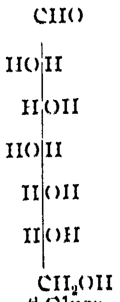
8



$$\begin{array}{r|l} \multicolumn{2}{c}{COOH} \\ H & OH \\ H & OH \\ HO & H \\ H & OH \\ H & OH \\ \multicolumn{2}{c}{CH_2OH} \end{array}$$

α-Gluco-
heptonic acid.

16



$$\begin{array}{r|l} \multicolumn{2}{c}{CHO} \\ HO & H \\ H & OH \\ HO & H \\ H & OH \\ H & OH \\ \multicolumn{2}{c}{CH_2OH} \end{array}$$

β-Gluco-
heptose.

he

B. *Third Class:*

$N = 16$ $a = 12$ i 4 r 6

When $R = R_1$, of the forms given under A, th

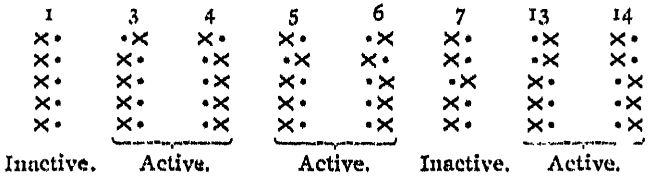
are identical:

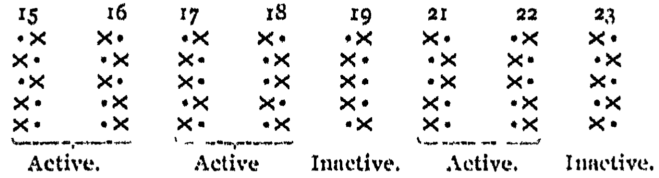
1 with 2
3 " 12
4 " 11
5 " 10
6 " 9
7 " 8

13 with 32
14 " 31
15 " 30
16 " 29
17 " 26

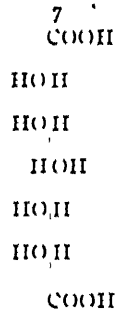
18 with
19 "
21 "
22 "
23 "

There remain then, as can be calculated from the formulas, sixteen configurations; *viz.*, six active pairs and four inactive forms. These are:

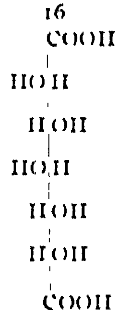




Of such configurations, the following are known:



α-Glucopentoxypimelic acid.
Inactive.



β-Glucopentoxypimelic acid.
Active.

A discussion of the methods and considerations leading to the determination of the positions O and OH as they have been developed by E. Fischer for the bodies of the sugar group, does not fall within the plan of this book.

Asymmetric Molecules with Chain Structure which contain a *double carbon linkage* must, in consequence of the resulting cis-trans isomerism, show *d*- and *l*-modifications for each of the two forms. According to Walden,[1] who called attention to these relations, the following bodies may be of this kind ·

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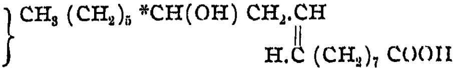
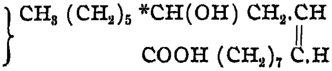
[1] Walden Ber. d. chem. Ges., 27, 3476.

Right-rotating ricinelaidic acid Trans form



$$\left.\right\} CH_3\ (CH_2)_5\ {}^*CH(OH)\ CH_2.\underset{\underset{H.C\ (CH_2)_7\ COOH}{\|}}{CH}$$

Right-rotating ricinoleic acid Cis form



$$\left.\right\} CH_3\ (CH_2)_5\ {}^*CH(OH)\ CH_2.\underset{\underset{COOH\ (CH_2)_7\ C.H}{\|}}{CH}$$

The left-rotating antipodes are as yet unknown.

Asymmetric bodies having a triple carbon linkage can yield only one pair of optical antipodes, thus, from the above acids only a single *d*-ricinstearoleic acid, corresponding to the formula[1]

$$CH_3.(CH_2)_5{}^*CH(OH)\ CH_2\ C \vdots C.(CH_2)_7.COOH,$$

may be obtained

Ring Structure Molecules—Those which contain only one asymmetric carbon atom yield *d*-, *l*-, and *r*-modifications, as has been already shown for many bodies, such as methyl-, ethyl-, and propylpiperidine, limonene, menthene, camphene, pinene, and others.

Cyclic compounds with two asymmetric carbon atoms may exist in four active isomeric forms, two of each being optical antipodes, and also in two racemic forms. As a matter of fact, these six forms are known in the case of the camphoric acids of which there exist, according to Aschan,[2] only (1) the common *d*-, *l*-, and *r*-camphoric acids which correspond to the maleinoid or cis form, and (2) the *d*-, *l*-, and *r*-isocamphoric acids which correspond to the fumaroid or cis-trans form. As is well known, the structure of camphoric acid has not been finally settled; the above relations point to the existence of two asymmetric carbon atoms. (Bredt's formula contains three, those of Tiemann and Semmler four, *C.)

The same conditions appear to obtain with other cyclic compounds, as, for example, borneol, the composition of which is not definitely known

Further details concerning the relations of optical modifications will be found in the chapter on the "Development of Active Isomers"

[1] Goldsobel Ber d chem Ges, 27, 3121.
[2] Aschan *Ibid*, 27, 2001

B. Physical and Chemical Behavior of the Optical Modifications

a BEHAVIOR OF THE ANTIPODES

17. Physical Properties.—Of these, only such can be different for the two antipodes in which the contrast of + and — is essentially inherent. Besides optical right and left rotation, and the enantiomorphism of crystals, the *pyroelectricity* of the latter belongs here The phenomenon of opposite electrical poles in a certain class of crystals is disclosed only when they are heated, or cooled, or subjected to one-sided strain or pressure. Among such, which in solid or dissolved condition show optical activity, the following have been found to exhibit pyroelectricity ·

Hexagonal System: quartz, potassium-lithium sulphate, sodium-lithium sulphate, potassium bromate, potassium periodate, *d*-antimonyl-strontium tartrate, *d*-lead tartrate.

Tetragonal System . *d*-antimonyl-barium tartrate

Monoclinic System *d*- and *l*-tartaric acid, *d*-potassium, ammonium and strontium tartrates, cane-sugar, milk-sugar, *d*- and *l*-carvoxime, *d*- and *l*-fenchone oxime, *d*- and *l*-*α*-carvone pentabromide.

For further information on the subject of pyroelectricity of crystals, the reader is referred to the excellent discussion of this condition in Liebisch's "Grundriss der physikalischen Krystallographie," 1896. pp 462 to 471

All other physical properties, on the contrary, are perfectly identical in the antipodes As observations on numerous substances have shown, this is the case with respect to

1. Specific gravity.
2. Melting-point and boiling-point.
3. Solubility.[1]
4. Heat of solution (*d*- and *l*-tartaric acid, Berthelot and Jungfleisch;[2] *d*- and *l*-inositol, Berthelot).[3]

---

[1] Certain statements are found concerning the unequal solubility of antipodes. At ordinary temperature *d*-asparagine is said to be somewhat more soluble than *l*-asparagine. (Piutti. Ber. d chem. Ges, 19, 1692.) In cooling down a hot aqueous solution of racemic camphoric acid, Jungfleisch observed, first the separation of the left-rotating, and then, below 40°, of right-rotating crystals. In dilute acetic acid the solubilities were even more different (Bull. Soc. Chim., [2], 41, 224). It is a question, in such cases, whether real antipodes were present or not.

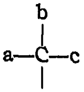
[2] Berthelot and Jungfleisch: Compt rend., 78, 711.

[3] Berthelot: *Ibid.*, 110, 1244

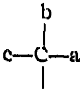
5. Heat of combustion (close agreement found for *d*- and *l*-camphoric acid, Louguinine;[1] *d*- and *l*-mannonic acid lactone, Fogh).[1]
6. Heat of neutralization (shown for *d*- and *l*-tartaric acid with active bases, Jahn).[2]
7. Electrical conductivity (*d*- and *l*-tartaric acid, Ostwald).[3]
8. Index of refraction (shown for *d*- and *l*-terpenes and derivatives, Wallach, Brühl)

18. Different Behavior of the Antipodes on Combination with Active Substances. Conditions of Solubility.—If the *d*- and *l*-forms of an active body be brought into new combinations which contain the original active complex, and in which no new asymmetric carbon atom is added, the two products are perfectly identical, with exception, of course, of their opposite rotating powers and crystalline enantiomorphism. This is the case when the antipodes of an acid are combined with an inorganic, or with an inactive organic base; the two salts show the same solubility, contain the same amount of water of crystallization, and so on

However, if the two oppositely rotating forms be brought into combination with an active substance, so that new asymmetric carbon atoms are added, then marked differences in behavior may appear. This is the case when a *d*- and *l*-acid are combined with the same alkaloid, or a *d*- and *l*-base with the same active acid, for example, with *d*-tartaric acid; the two salts differ, especially in their solubilities. The reason for this is found simply in the fact, that when a right and left asymmetric group,

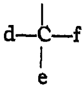


$$\begin{array}{c} \text{b} \\ | \\ \text{a—C—c} \\ | \end{array}$$



$$\begin{array}{c} \text{b} \\ | \\ \text{c—C—a} \\ | \end{array}$$

are attached to the same asymmetric complex,



$$\begin{array}{c} | \\ \text{d—C—f} \\ | \\ \text{e} \end{array}$$

the two resulting bodies

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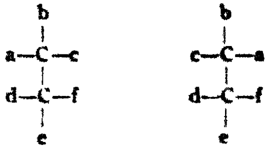
[1] Louguinine, Fogh, see Stohmann Ztschr. phys Chem, 6, 334, and 10, 410.
[2] H Jahn Wied Ann, 43, 306
[3] Ostwald Ztschr phys Chem, 3, 371



are no longer mirror images of each other.

The unequal solubility of two such isomeric combinations does not appear to bear any definite relation to the direction of rotation of the active components. When the same alkaloid is united to different active acids, sometimes the *d*-form of the latter, and sometimes the *l*-form, gives the least soluble salt, that is, the one which precipitates first. In the same manner *d*-tartaric acid behaves differently with the antipodes of different bases. This is shown by the following observations which in the main have been taken from a table by Winther.[1] The symbols (*W*) and (*A*) indicate the solvent, water or alcohol:

d-Cinchonicine	precipitates	*l*-tartaric acid (*W*)
d-Cinchonine	"	*l*-tartaric acid (*W*)[3]
d- "	"	*l*-cinnamic acid dibromide (*A*)[4]
d- "	"	*d*-methoxysuccinic acid (*W*)[5]
d- "	"	*d*-mandelic acid (*W*)[6]
d- "	"	*d*-isopropylphenylglycolic acid (*A*)
d- "	"	*d*-phenylbromlactic acid (*A*)[8]
d-Quinidine	"	*d*-cinnamic acid dibromide (*A*)[9]
d-Quinicine	"	*d*-tartaric acid (*W*)
l-Quinine	"	*d*-tartaric acid (*W*)
l- "	"	*d*-tropic acid (*W*)
l- "	"	*l*-isopropylphenylglycolic acid (*A*)[13]
l-Cinchonidine	"	*d*-ethoxysuccinic acid (*W*)[14]

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[1] Winther, Ber. d. chem. Ges. 28, [illegible]

[2] Pasteur, Compt. rend. 37, 162.

[3] Pasteur, Ann. chim. phys. [3] 38, 437.

[4] Erlenmeyer, Jr., Ann. Chem. (Liebig) 271, [illegible]; Ber. d. chem. Ges. 26, 1659. Liebermann, Ibid., 26, 1662; Hirsch, Ibid., 27, 883.

[5] Purdie and Marshall, J. Chem. Soc. 63, 217.

[6] Lewkowitsch, Ber. d. chem. Ges. 16, 1574 and [illegible]

[7] Fileti, Gazz. chim. ital. 22, 2, 395; J. prakt. Chem. [2] 46, 560.

[8] Erlenmeyer, Jr., Ann. Chem. (Liebig) 271, [illegible]; Ber. d. chem. Ges. 24, 2830, 26, 1659.

[9] Hirsch, Ber. d. chem. Ges. 27, 883.

[10] Pasteur, Compt. Rend., 37, 162.

[11] Pasteur, Ann. chim. phys., [3] 38, 437.

[12] Ladenburg and Hundt, Ber. d. chem. Ges. 22, 2590.

[13] Fileti, *Loc cit.*

[14] Purdie and Walker, J. Chem. Soc., 63, 229.

l-Cinchonidine	precipitates	*l*-cinnamic acid dibromide (benzene),[1]
l- "	"	*l*-allocinnamic acid dibromide (benzene);[2]
l-Strychnine	"	*d*-pyrotartaric acid (*W*),[3]
l- "	"	*d*-galactonic acid (*W*),[4]
l- "	"	*d*-dihydro-o-phthalic acid (*W*),[5]
l- "	"	*d*-cinnamic acid dichloride (*A*),[6]
l- "	"	*d*-cinnamic acid dibromide (*A*),[7]
l- "	"	*l*-lactic acid (*W*),[8]
l- "	"	*l*-methoxysuccinic acid (*W*),[9]
l- "	"	*l*-propoxysuccinic acid (*W*);[10]
l-Brucine	"	*d*-tartaric acid (*A*),[11]
l- "	"	*d*-α-oxybutyric acid (*W*),[12]
l- "	"	*d*-α-β-cinnamic acid dibromide (*A*),[13]
l- "	"	*d*-phenyl-β-γ-dibrombutyric acid (*A*),[14]
l- "	"	*l*-valerianic acid (*W*);[15]
d-Tartaric acid	"	*d*-α-pipecoline (*W*),[16]
d- " "	"	*d*-ethylpiperidine (*W*),[17]
d- " "	"	*d*-conine (*W*),[18]
d- " "	"	*d*-copellidine (*W*),[19]
d- " "	"	*d*-tetrahydroquinaldine (*W*),[20]
d- " "	"	*l*-β-pipecoline (*W*),[21]
d- " "	"	*l*-isocopellidine (*W*),[22]
d- " "	"	*l*-propylenediamine (*W*),[23]
d- " "	"	*l*-1,5-tetrahydronaphthylenediamine (*W*).[24]

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[1] Hirsch *Loc cit*

[2] Liebermann Ber d chem Ges, **27**, 2042

[3] Ladenburg *Ibid*, **28**, 1170

[4] Fischer and Hertz *Ibid*, **25**, 1257

[5] Proost *Ibid*, **27**, 3185

[6] Liebermann and Finkenbeiner *Ibid*, **26**, 683, Finkenbeiner · *Ibid.*, **27**, 880

[7] Loth. Meyer, Jr *Ibid*, **25**, 3121, Liebermann *Ibid*, **26**, 245; Liebermann and Hartmann *Ibid*, **26**, 829 and 1665

[8] Purdie and Walker J Chem. Soc, **61**, 754

[9] Purdie and Bolam *Ibid*, **67**, 944

[10] *Ibid*

[11] Pasteur Ann chim phys, [3], *loc cit.*

[12] Guye and Jordan Compt rend., **120**, 562

[13] Hirsch *Loc cit*

[14] Loth Meyer, Jr, and Stein Ber d chem Ges, **27**, 890.

[15] Schutz and Marckwald *Ibid*, **29**, 52.

[16] Ladenburg Ann Chem (Liebig), **247**, 64

[17] *Ibid*, p 71

[18] *Ibid*, p 85

[19] Levy and Wolffenstein Ber d. chem. Ges, **28**, 2270.

[20] Ladenburg *Ibid*, **27**, 76

[21] *Ibid*, p 75

[22] Levy and Wolffenstein *Loc cit*

[23] Baumann Ber d chem. Ges., **28**, 1179.

[24] Bamberger *Ibid*, **23**, 291

In the above list there are nineteen cases in which bases an acids of opposite rotation unite to form a less soluble salt, an seventeen cases in which the salt is formed by the union c acids and bases of like rotation

In the two groups of isomeric cinchona alkaloids their com position appears to play some part as may be seen from th following table in which is given the modifications of severa acids which yield the less soluble salts with the bases·

	Bases $C_{19}H_{22}N_2O$			Bases $C_{20}H_{24}N_2O_2$.		
	Cinchonine	Cinchonicine	Cinchonidine	Quinicine	Quinidine	Quinine
Tartaric acid	*l*	*l*	—	*d*	—	*d*
Phenyldibrompropionic acid	*l*	—	*l*	—	*d*	—
Isopropylphenylglycolic acid ...	*d*	—	—	—	—	*l*
Methoxysuccinic acid	*d*	—	*d*	—	—	—

From this it might appear that the bases of each group behave in a similar manner with each acid and also that the two groups are opposed to each other in their action; if the one combines with the *d*-form of an acid the other takes the *l*-form However, a greater number of observations will be required to fully establish the rule

Ch. Winther has proposed a theory concerning the resolution of racemic bodies by active bases which takes into consideration the configuration of the molecules.[1] Reference only can be made to this here.

For the application of the unequal solubilities of the salts of active bases and acids in splitting racemic bodies, see § 33

19. **Physiological Differences between the Antipodes.**—These are recognized through the following phenomena

1. *By the power which certain organized ferments possess, when growing in solutions of racemic bodies, to destroy one component of the combination while the other is left unchanged*

This power belongs especially to a number of molds, such as

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[1] Ch. Winther Ber. d. chem Ges, 28, 3000

Penicillium glaucum, *Mucor Mucedo*, *Aspergillus fumig* and others, also to several kinds of yeast, and finally to ce schizomycetes (*Bacterium termo*, *Bacillus ethaceticus* others) The first observations on this point were mac Pasteur[1] in 1860, who found that if spores of *Penici glaucum* along with traces of nutritive salts (potassium phate and magnesium sulphate) are sown in a soluti ammonium racemate, the originally inactive liquid bec gradually levorotatory as the development of the fungu ceeds and that finally no dextrotartaric acid whatever is It was observed later that solutions of many other ra bodies in contact with fungi behave in the same manner consequently that from them in some cases the right-rot and in other cases the left-rotating form could be secured this way it was found possible to obtain active forms fr number of racemic acids, as lactic acid, aspartic acid, mar acid, and even from haloid acids, for example from cinr acid dichloride, also from several alcohols, as methyle carbinol, methylpropylcarbinol, propyleneglycol, and o (see § 34). With many substances, however, the growt fungi is not possible and they remain in the inactive cond

Further data concerning the methods employed in experiments, and a description of the fungi, will be founc 34.

In the following the question of the mode of action o fungi, and whether any definite rules may be deduced, w taken up first It must be remarked at the outset, how concerning observations in this direction, that many of date from a time when methods of producing pure cul of the fungi had been but little developed and that wit doubt many experiments were carried out with impure mat The results, therefore, can not be looked upon as fully e lished in all cases.

As far as the molds are concerned, it does not appear different varieties possess any definite selective action o antipodes. It has been found on the contrary that the mold decomposes the right modification of some racemic bo and the left modification of others. For example, by th of *Penicillium glaucum*, the following active forms w obtained from racemic bodies[1]

---

[1] Pasteur Compt rend., 51, 298.

d-methylethylcarbin carbinol,
d-ethylidene lactic acid,
d-ethoxysuccinic acid,
d-mandelic acid,
d-aspartic acid,[2]
d-leucine,[3]
l-methylethylcarbinol,
l-methylpropylcarbinol,
l-ethylpropylcarbinol,
l-tartaric acid,
l-mannonic acid lactone,
l-glutaminic acid,[4]
l-glyceric acid

As seen, the destructive action of the fungus on the alcohol as well as on the acids, is exerted in some instances on the o form, and in others on the opposite.

There are some cases in which from racemic bodies, t dextro form may be obtained by one variety of fungus and t levo form by aid of a different fungus Thus, there are n attacked

d-Mandelic	acid	by	*Penicillium glaucum*, *Mucor Mucedo*
l-	"	"	" *Saccharomyces ellipsoideus* and another schizomycite not definitely known (vibrio[5])
d-Glyceric	acid[6]	"	*Bacillus ethaceticus*[7]
l-	"	"	" *Penicillium glaucum*[8]
d-Tartaric	"	"	a certain unnamed schizomycite (vibrio[9])
l-	"	"	" *Penicillium glaucum*[10]

The investigations of E Fischer have thrown much lig on the action of yeasts (*Saccharomyces ellipsoideus*, *cerevisiae*, *S. Pastorianus*, *S Marxianus*, etc.) on t different kinds of sugars It was found, that of the tv antipodes, only one undergoes fermentation, while the oth remains unchanged. Thus:

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[1] The literature of these data will be found in § 34

[2] The hydrochloric acid solution of the *l*-form, which in water shows dext rotation, was not attacked.

[3] The form rotating to the left in hydrochloric acid, and in water to the rig was obtained

[4] The form rotating to the left in hydrochloric, and in the same direction wh dissolved in water, was left

[5] Lewkowitsch Ber d chem Ges, **15**, 1505, **16**, 1568.

[6] The racemic calcium glycerate used, left the levorotating salt which correspon to the dextro acid

[7] Frankland and Frew, J Chem. Soc, **59**, 101

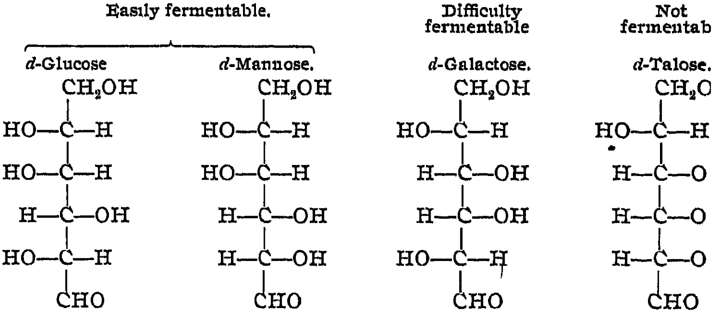
[8] Lewkowitsch Ber d. chem Ges, **16**, 2720

[9] Lewkowitsch *Loc. cit*

[10] Pasteur, LeBel

Ferment	Do not ferment
d (+) Glucose,	l (—) Glucose,[1]
d (+) Mannose,	l (—) Mannose,[2]
d (+) Galactose,	l (—) Galactose,[3]
d (—) Fructose,	l (+) Fructose[4]

Again, it was found that with isomeric sugars which shc the same direction of rotation the configuration of the mol cule exerts an influence on the behavior toward yeast. Fisch and Thierfelder[5] have found the following differences



2. *Unorganized Ferments* (*Enzymes*) show in their pow of splitting glucosides phenomena similar to those of tl yeasts. Investigations of E. Fischer have shown that tl hydrolysis of the α- and β-isomeric forms (different configur tions) of *d*- and *l*-methyl glucoside may depend on (1) tl nature of the enzyme, (2) the configuration of the glucosid and (3) the direction of rotation of the active group. The fc lowing relations have been observed:[6]

	Emulsin.	Invertin.
α-Methyl, *d*-glucoside..........	does not split	splits
α- " *l*- "	does not split	does not split
β- " *d*- "	splits	does not split
β- " *l*- "	does not split	—

---

[1] Fischer Ber d chem. Ges., **23**, 2621; **27**, 2031

[2] Fischer: *Ibid.*, **23**, 382

[3] Fischer: *Ibid*, **25**, 1259.

[4] Fischer *Ibid.*, **23**, 389

[5] Fischer and Thierfelder: *Ibid*, **27**, 2035.

[6] Fischer: *Ibid.*, **27**, 2985; **28**, 1429.

Finally, as regards the explanation of the behavior of the pure enzymes, as well as of that of the fungi containing enzymes, there can be but little doubt that here the same conditions obtain as in the case of bringing together racemic acids and alkaloids The enzymes, like all other albuminous bodies, represent asymmetric molecules endowed with rotating power, and therefore behave differently with the optical antipodes. Pasteur,[1] many years ago, employed an illustration when he remarked that if a right and left screw be driven into pieces of wood, the fibers of which run in a straight direction (inactive substance), two systems of the same kind are produced; but that this is no longer the case if the fibers of the wood themselves possess a spiral form, and turned in opposite directions in the two pieces Again, as regards the unequal action of molecules of different configurations, it appears that the yeast cells with their asymmetrically formed active agent attack and ferment only those kinds of sugars whose geometry is not too greatly different from that of grape-sugar (Fischer and Thierfelder[2]) In the same way, one can represent the action of the enzymes on glucosides as taking place, only when the geometric forms are such as to permit that close approach of the molecules necessary to the beginnings of chemical change. To employ a figure used by Fischer,[3] the two bodies must fit each other as lock and key. What becomes of the part of the active substance taken up by the organized ferment, is known only in the case of a few fermentations; for all other cases there are no available observations

3 Further physiological differences between optical antipodes have been observed in a few instances with reference to *toxicity* and *taste*

Different Degrees of Toxicity between d- and l-Tartaric Acid were noted by Chabrié[4] by injecting solutions of 1 part of acid to 5 or 6 parts of water into the peritoneal cavity of guinea pigs and observing the time required to produce death. From the experiments which were extended to include racemic and mesotartaric acids, inactive modifications, it was found that the toxicity of the different acids calculated for equal weights of animal were as follows:

---

[1] Pasteur "Dissymmetrie moleculaire," 1860

[2] Fischer and Thierfelder Ber. d chem Ges, **27**, 2036

[3] Fischer *Ibid*, **27**, 2992

[4] Compt rend, **116**, 1410

Left tartaric acid	31
Right tartaric acid	14
Racemic acid	8
Mesotartaric acid	6

According to this, *l*-tartaric acid is about twice as strong a poison as the *d*-acid.

With conine, Ladenburg[1] noticed no difference in toxicity between the natural right-rotating base and the synthetic racemic α-propylpiperidine.

A difference in taste between *d*- and *l*-asparagine has been noted In evaporating an aqueous solution of 20 kilograms of asparagine obtained from vetch shoots, Piutti[2] noticed the formation of enantiomorphous crystals, which, when separated from each other mechanically, were found to be characterized by equal and opposite rotations, and further by the fact that the right-rotating crystals had a sweet taste, while those rotating to the left had the very slight taste of the common asparagine. In derivatives from the two forms, such as *d*- and *l*-aspartic acid a difference in taste was no longer noticed. The equal rotations of the two forms indicate that the two asparagines are real optical antipodes. A second example is given by glutaminic acid, the *d*-form of which has a specific taste while the *l*-form is tasteless.[3] Pasteur[4] has made the suggestion that the differences in taste may be due to the nerves themselves being formed of asymmetric substances, and that an effect exists here like that of the ferments

b. PROPERTIES OF RACEMIC COMPOUNDS AND DISTINCTIONS BETWEEN THESE AND ACTIVE MODIFICATIONS.

The inactive racemic bodies obtained in various ways (see § 27 to 33) may be in part definite chemical compounds (symbol *r*) or mechanical mixtures of the active antipodes (symbol *d l*).[5] In both cases they may be split up into the latter.

As definitely characterizing racemic compounds the following relations may be taken into consideration, which show, first, the differences between them and the active modifications, and which, secondly, permit in given cases a determination of the question as to which is present, a compound or mixture of the antipodes.

---

[1] Ladenburg Ann Chem. (Liebig), **247**, 83

[2] Piutti· Ber. d. chem Ges, **19**, 1691; Gazz chim. ital., **17**, 126, 182.

[3] Menozzi and Appiani Acc. d. Lincei, 1893, II, 421.

[4] Pasteur: Compt rend, **103**, 138.

[5] Following the suggestion of E. Fischer· Ber. d. chem. Ges., **28**, 1153.

1. Crystallized Racemic Compounds

20. Molecular Weight.—It was attempted to show by cryoscopic methods that racemic bodies have twice the molecular weight of the antipodes, but without success. It was found that equally strong solutions of active and inactive forms always cause the same depression of the freezing-point, and therefore that the racemic forms in solutions separate into their components This was observed first by Raoult[1] with racemic and tartaric acids (under 5 parts to 100 of water), also with their sodium-ammonium salts, and later in still other cases, as with the dimethyl esters of diacetyl racemic acid, diacetyl tartaric acid,[2] isonitrosodipentene and isonitrosolimonene dissolved in glacial acetic acid.[3] The identity of equally diluted solutions of racemic acid with *d*- and *l*-tartaric acid was found further in the agreement of the specific gravities,[4] the electrical conductivity,[5] and magnetic rotation.[6]

The determination of vapor-density proved of equally little value Anschütz[7] found that diethyl racemate and *d*-tartrate have the same vapor-density, and consequently that the first substance, in case it exists as a racemic compound in liquid form, must have broken down into the two tartrate esters With the solid dimethyl racemate, whose melting-point (85°) is markedly different from that of the tartrate ester (45°), the decomposition appears to take place at the boiling temperature (158° at 11.5 mm.), because this is the same for the two bodies

In view of the fact that the densities of diethyl racemate and tartrate in liquid condition are the same, I. Traube[8] comes to the conclusion, aided by the atomic constants proposed by him,[1] that the molecules of all three bodies are simple, and therefore, that the liquid ethyl racemate is a mixture of the two tartrate esters.

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[1] Raoult Ztschr phys Chem, **1**, 186

[2] Pulfrich: See Anschütz Ann Chem (Liebig), **247**, 121.

[3] Wallach· *Ibid*, **246**, 231.

[4] Perkin J. Chem Soc, **52**, 362, Marchlewski. Ber d chem Ges, **25**, 1556

[5] Ostwald. Ztschr phys Chem, **3**, 371

[6] Perkin *Loc cit*

[7] Anschutz Ber d chem Ges, **18**, 1397

[8] I Traube: *Ibid*, **29**, 1394.

In the same way, Traube draws the conclusion from the densities of the crystalline racemic acid and tartaric acid, that both bodies have the same molecular weight, which corresponds to the formula $(C_4H_6O_6)_2$. This reaction of changing solid racemic acid or its salts into the mixture of tartrates (see §27) would not, therefore, be represented by $d + l = dl$, but by $dd + ll = 2dl$.

21. Crystalline Form and Water of Crystallization.—In the union of enantiomorphous antipodes to form a racemic compound, the following cases may appear

1. A body of different composition may be formed by the loss or addition of water of crystallization. A change in crystalline form naturally results with this[2]

For example

Tartaric and racemic acid	Crystalline form
Active, $C_4H_6O_6$	monoclinic-hemimorphous
Racemic, $C_4H_6O_6 + H_2O$	triclinic-holohedral

Sodium-ammonium tartrate and racemate	Crystalline form
Active, $NaNH_4C_4H_4O_6 + 4H_2O$	rhombic-hemihedral
Racemic, $NaNH_4C_4H_4O_6 + H_2O$	monoclinic-holohedral

2 The composition may remain unchanged. Even then, as observation has shown, the crystals of the racemic compound belong to a crystalline group different from that of the active forms. For example

Sodium tartrate and racemate	Crystalline form
Active, $Na_2C_4H_4O_6 + 2H_2O$	rhombic-hemihedral
Racemic, $Na_2C_4H_4O_6 + 2H_2O$	monoclinic-holohedral

Carvonetetrabromide	Crystalline form.
Active, $C_{10}H_{14}Br_4O$	rhombic-hemihedral
Racemic, $C_{10}H_{14}Br_4O$	monoclinic-holohedral.

It appears that in some unusual cases the crystalline system may remain unchanged, the group only being altered. For example:

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[1] Traube Ber d chem. Ges, **28**, 2724, 2728, 2924, **29**, 1023

[2] These data are from Rammelsberg's "Handbuch der kryst and phys Chemie," Vol II (1882), and from Liebisch's "Grundriss der phys Kryst." (1896)

Potassium antimonyl tartrate and racemate	Crystalline form
Active, $KSbOC_4H_4O_6 + \frac{1}{2} H_2O$	rhombic-hemihedral.
Racemic, $KSbOC_4H_4O_6 + \frac{1}{2} H_2O$	rhombic-holohedral

While the active antipodes belong always to one of the 11 crystalline groups described in § 5 the racemic forms are always found in one of the 21 of the 32 possible groups in which hemihedral forms are excluded. In these differences we have the most decided characteristics of true racemic compounds.

The amount of water of crystallization in racemic forms may be the same or greater or less than in the active forms. In these relations there is no fixed rule. We have, for illustration

			Racem	Active
Tartaric and racemic acid,	$C_4H_6O_6$	+	H_2O	—
Ammon. tartrate and racemate,	$(NH_4)_2 C_4H_4O_6$	+	$2H_2O$	—
Potass tartrate and racemate,	$K_2C_4H_4O_6$	+	$2H_2O$	$\frac{1}{2}H_2O$
Sodium tartrate and racemate,	$Na_2C_4H_4O_6$	+	$2H_2O$	$2H_2O$
Thallium tartrate and racemate,	$Tl_2C_4H_4O_6$	+	—	$\frac{1}{2}H_2O$
Sod -ammon tartrate and racemate,	$Na(NH_4)C_4H_4O_6$	+	H_2O	$4H_4O$
Potass. lithium tartrate and racemate,	$KLiC_4H_4O_6$	+	H_2O	H_2O
Potass antimon tartrate and racemate,	$KSbOC_4H_4O_6$	+	$\frac{1}{2}H_2O$	$\frac{1}{2}H_2O$
Calcium mannonate,	$Ca(C_6H_{11}O_7)_2$	+	—	$2H_2O$[1]
Strontium glycerate,	$Sr(C_3H_5O_4)_2$	+	$\frac{1}{2}H_2O$	$3H_2O$[2]
Barium glycerate,	$Ba(C_3H_5O_4)_2$	+	$\frac{1}{2}H_2O$	$3H_2O$[2]

22. **Density.**—The specific gravities of the active isomers and of the racemic form of a number of crystalline bodies have been determined by Liebisch[3] and by Walden.[4] The observations have shown that the densities for the *d*- and *l*-modifications, which were always found to be the same, were in most instances smaller than that for the corresponding racemic form. In some cases the reverse was found to be true, while perfect agreement may also occur In the following table, which presents these three cases, the amount of increase or decrease in passing from the active to the racemic form is given The observations by Walden give values of d_4^{20}:

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[1] Fischer Ber d chem Ges., **23**, 378

[2] Frankland and Appleyard J Chem Soc, **63**, 310 The Li, Mg, Ca, Zn and Cd salts of active and racemic glyceric acid have the same water of crystallization.

[3] Liebisch (see Wallach) Ann, Chem (Liebig), **286**, 139

[4] Walden Ber d chem Ges, **29**, 1692

	Active forms	Racemic form	Change in per cent	Observe
Tartaric acid, anhydrous racemic acid	1.759	1 788	+ 1 7	L.
Tartaric acid, anhydrous racemic acid	1.755	1.778	+ 1 3	W. P
Malic acid	1 595	1 601	+ 0.4	W.
Camphoric acid	1 188	1.228	+ 3.4	W.
Isocamphoric acid	1 243	1 249	+ 0.5	W.
Limonene (dipentene) tetrabromide	2 134	2 225	+ 4.3	L.
Carvoxime	1 108	1 126	+ 1 6	L
Fenchoneoxime	1.117	1 142	+ 2 2	L.
β-Isofenchoneoxime	1 134	1 180	+ 4 1	L.
Carvone tetrabromide from carvone[1]	2 2428	2 2495	+ 0 3	L
Sobrerol	1.128	1.131	+ 0 3	L
Chlorsuccinic acid	1.687	1 679	— 0 5	W
Bromsuccinic acid	2 093	2 073	— 1.0	W
Glutaminic acid	1 538	1 511	— 1 8	W
Mandelic acid	1 341	1 300	— 3 1	W.
Carvone tribromide from hydrocarvone	1 958	1.958	0	L

In those cases in which the specific gravity of the racemic bodies is greater or less than those of the components, it may be safely assumed that the first represent true chemical compounds. If they were merely mechanical aggregations, the same behavior should be expected as with isomorphous mixtures, the densities of which, as is well known, are additive properties, that is, as the densities of the isomers are the same, that of the raceme body should also be the same. A contraction or dilatation, on the contrary, points to chemical combination

23. **Solubility.**—As far as observations have shown the racemic compounds, as a rule, are less readily soluble than the active forms. Numerical results have been given for the following substances:

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[1] Perkin J Chem Soc, 51, 366

100 Parts of solvent dissolve at t°.

	t°	Active forms	Racemic form.	Observer.
Tartaric acid and anhydrous racemic acid in water.	0°	115.0 pts	8.2 pts.	Leidié: C. r., 95, 87
	20	139.4 “	17.0 “	
	40	176.0 “	37.0 “	
	60	217.6 “	64.5 “	
	80	273.3 “	98.1 “	
	100	343.5 “	137.8 “	
Glyceric acid salts (anhydrous) in water: $Mg(C_3H_5O_4)_2$	20	43.05 “	22.78 “	Frankland and Appleyard. J. Chem. Soc., 63, 310
Ca “	20	9.32 “	3.85 “	
Ba “	20	50.15 “	6.60 “	
Zn “	20	39.03 “	3.87 “	
Cd “	20	85.00 “	4.43 “	
Potassium methoxysuccinate in water.	16	*d* 14.4, *l* 13.9	3.0 “	Purdie and Walker J. Chem. Soc., 63, 222, 233
Calcium methoxysuccinate in water.	14	5.41 “	0.46 “	
Calcium ethoxysuccinate in water	15	4.15 “	0.63 “	
Calcium gulonate in water	15	5.8 “	1.6 “	E. Fischer Ber., 25, 1028
Calcium galactonate, in water	100	50 “	2.2-2.5 “	E. Fischer and Hertz Ber., 25, 1253
Leucine in water	—	2.44 “	0.98 “	Walden: Ber., 29, 1702
Inosite in water	—	ca. 50 “	4.56 “	Walden: Ber., 29, 1702.
Camphoric acid in water	20	6.96^1 “	0.239^2 “	[1] Jungfleisch [2] Aschan From Beilstein, Org. Ch.
“ “ alcohol	15	112 “	33 “	
Isocamphoric acid in water	20	0.347 “	0.203 “	Aschan: Stud. Campher-gruppe.
Camphoronic acid in water	20	16.8 “	3.72 “	Aschan: Ber., 28, 16.
Isopropylphenylglycolic acid in alcohol	13	47.4 “	21.6 “	Fileti J. prakt. Chem., [2], 46, 561

The lower solubility of the racemic compounds is shown in many cases by the formation of a crystalline precipitate when concentrated solutions of the active forms are mixed. This is true, for example, of concentrated aqueous solutions of tartaric acids (Pasteur),[1] of alcoholic solutions of camphoric acids (Chautard)[2] and of many derivatives of the limonenes as the nitrosochlorides, nitrosates, hydrochlornitrolbenzylamines, hydrochlornitrolanilides, dissolved in alcohol (Wallach),[3] and the α-nitrolpiperidines dissolved in petroleum ether (Wallach). Likewise, from a mixture of the methyl alcohol solutions o *d*- and *l*-dimethyl tartrate, the less soluble racemate este crystallizes at once (Anschütz).[5]

This rule of the lower solubility of the racemic compound is, however, not without exceptions. Thus, the two activ α-limonenebenzoylnitrosochlorides are less soluble in aceti ether than the crystalline dipentene compound (Wallach). 8.64 parts of the active mandelic acid, and 15.97 parts of th racemic acid dissolve in 100 parts of water at 20 (Lewkowitsch).[7] 100 parts of water dissolve only 0.084 par of *l*-silver valerate at 20°, but 1.181 parts of the racemic sal at the same temperature (Schutz and Marckwald).[8] *d*- and *l* dimethyldiacetyltartrates are less soluble in benzene, than th diacetylracemate ester (Anschutz).[9] *d*- and *l*-barium cam phoronates form difficultly soluble precipitates, while the *r*-sal is easily soluble in water (Aschan).[10] Nearly complete agreement in solubility was found for *d*- and *r*-coniine, 100 parts o water dissolving 1.80 parts of the first and 1.93 parts of th second at 19.5° (Ladenburg).[11]

The solubility of the racemic compounds may be modifie also by the fact, that even in a concentrated solution they ar not in unchanged condition, but are partly dissociated int their antipodes. This has been shown for racemic acid, a mentioned, and also for its sodium-ammonium salt which, eve in strong aqueous solution, may be completely split up int the two tartrates. See §27. Temperature of Transformatio

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[1] Pasteur Dissymmetrie moleculaire, 1860

[2] Chautard Compt rend, **56**, 698

[3] Wallach Ann Chem (Liebig), **270**, 195

[4] Wallach *Ibid*, **252**, 125

[5] Anschutz Ber d chem Ges, **18**, 1398

[6] Wallach Ann. Chem (Liebig), **270**, 177

[7] Lewkowitsch Ber d chem Ges, **16**, 1566

[8] Schütz and Marckwald *Ibid*, **29**, 58

[9] Anschutz Ann. Chem (Liebig), **247**, 116

[10] Aschan Ber d chem Ges, **28**, 16

[11] Ladenburg. *Ibid*, **28**, 165

24. Melting-Point.—The determinations of the melting-points of active and racemic forms of many crystallizable substances have failed to show any regularities. In some cases, the melting-point of the racemic compound is higher than that of the active components, while in other cases the reverse is true. The melting-points may also be the same. As may be seen from the table below, quite different groups of bodies are found in each of the three classes:

	Active forms	Racemic form	Diff.	Observer
A. Melting-point higher for the racemic than for the active form.				
Tartaric acid, racemic acid $+H_2O$	170°	204°	34°	Walden: Ber., 29, 1701.
Malic acid	100	130.5	30.5	Walden: Ber., 29, 1698.
Dimethyl tart. and racem.	45	85	40	Anschütz: Ber., 18, 1307.
Methoxysuccinic acid	89	108	19	Purdie and Marshall: Ch. Soc. 63, 217
Isopropylphenylglycolic acid	153.5	156.5	3	Filetti: Gazz. ch., 22, II, 395
Galactonic acid, lactone	90 92[1]	122 125[2]	33	[1]Schnelle and T.: L. Ann., 271, 83 [2]Fischer: Ber., 25, 1247
Mannitol	163.5	168	4.5	E. Fischer: Ber., 23, 370, 383
Mannoheptitol	187	203	16	Smith: L. Ann., 272, 189.
Mannonic acid, phenylhydrazide	215	230	15	E. Fischer: Ber., 23, 378.
Mannoheptonic acid, phenylhydrazide	220	225	5	Smith: L. Ann., 272, 185, 186
Mannoheptosephenylosazone	203	210	8	Smith: L. Ann., 272, 187, 188.
Galactosephenylosazone	195	206	11	E. Fischer: Ber., 25, 1256.
Gulonic acid, phenylhydrazide	148	154	6	E. Fischer: Ber., 25, 1029.
Camphoric acid	187	202	15	Walden: Ber., 29, 1700.
Isocamphoric acid	171.5	190.5	19	Walden: Ber., 29, 1701.
Limonenetetrabromide	105	124	19	Wallach: Ber., 24, 1559.
Limonene-α-nitrolpiperidide	94	154	60	Wallach: Ber., 24, 1559.

	Active forms	Racemic form	Diff	Observer
Limonene-β-nitrolpiperidide	1110°	152°	42°	Wallach Ber., 24, 1559
Limonene-α-nitrolanilide	113	126	13	Wallach . Ber , 24, 1559
Limonenecarvoxime	72	93	21	Wallach Ber., 24, 1559
Limonenehydrochlornitrolanilide	117.5	140	22.5	Wallach L Ann , 270, 194.
Limonene-α-nitrolbenzylamine	92.5	109.5	17	Wallach . L. Ann., 270, 192
Limonenehydrochlornitrolbenzylamine	03.5	150	46.5	Wallach . L Ann , 270, 192.
Fenchone-β-isoxime	137	160.5	23.5	Wallach : L Ann , 272, 108
Fenchylphenylsulfourea	152.5	169.5	17	Wallach · L. Ann , 272, 108
β-Carvonepentabromide	86.5	97	10.5	Wallach L Ann , 286, 123
Caronesemicarbazide	168	178	10	Baeyer Ber , 28, 640
α-Pipecolinehydrochloride	190	205	15	Marckwald . Ber , 29, 46
α-Pipecolinepicrate	116.5	127.5	11	Marckwald : Ber , 29, 46.

B Melting-point of the racemic lower than for the active forms.

Chlorsuccinic acid	176°	153.5°	22.5°	Walden · Ber , 29 1699
Bromsuccinic acid	172	160.5	11.5	Walden Ber., 29, 1699
Glutaminic acid	202	198	4	Walden Ber , 29, 1700
Mannoheptonic acid, lactone	*d* 149 *l* 154	85	67	Fischer and Smith · L. Ann , 272, 182
Glucosediphenylhydrazone	162.5	132.5	30	Fischer · Ber., 23, 2620.
Mannoheptose-phenylhydrazone	196–200	175.5	23	Fischer. Ber., 23, 2226; L. Ann , 272, 182.
Mannitoltribenzacetal	207	191	16	Fischer: Ber., 27, 1524.
Mandelic acid	132.8	118	14.8	Lewkowitsch: Ber., 16, 1566.
Limonene-β-nitrolanilide	153	149	4	Wallach. Ber., 24, 1559.
" -hydrochlorcarvoxime	135	125	10	Wallach: Ber., 24, 1559.
" α-benzoylnitrosochloride	109.5	90	19.5	" L. Ann., 270, 17

	Active forms	Racemic form.	Diff.	Observer
Fenchylalcohol	40°	34°	6°	Wallach: L Ann., 272, 108.
" -oxime	160.5	159	1.5	" L Ann., 272, 108.
" -α-isoxime	114.5	98.5	16	" L. Ann., 272, 108.
Oxybenzylidene-fenchylamine	95	64.5	30.5	" L Ann., 272, 108.
β-Carvonetetrabromide ...	121	108	13	" L Ann., 286, 121.
α-Carvonepentabromide...	142.5	125	17.5	" L. Ann., 286, 122.
Carvonesemicarbazide	162.5	155	7.5	v. Baeyer: Ber., 28, 640.
α-Pipecoline salts,				
$C_6H_{13}N\ HAuCl_4$	131.5	118.5	13	Marckwald. Ber., 29, 46
$(C_6H_{13}N)_2\ H_2PtCl_6$ ...	194	186	8	Marckwald. Ber., 29, 46.
$(C_6H_{13}N\ HI)CdCl_2$ ...	147	131	16	Marckwald Ber., 29, 46.

C Melting-points of the active and racemic forms the same.

Galactonic acid phenylhydrazide	200°–205°	Fischer. Ber., 27, 3225
Gulonic acid, phenylhydrazide	147–149	Fischer Ber., 27, 3225
Phenylgulosazone .. .	157–159	Fischer Ber., 25, 1030
Limonene-α-nitrosochloride .. .	103–104	Wallach L Ann., 252, 111, 125
π-Monobromcamphor	92.4–92.7	Kipping and Pope J Chem Soc., 67, 372

In the cases of those racemic bodies whose melting-points are found to be lower than those of the components there is the possibility that they are not compounds but mixtures, as this relation is characteristic of mixtures In fact this has been proved in the case of gulonic acid lactone. A mixture of equal parts of the antipodes gave on evaporation of the aqueous solution at first an inactive crystal mass, the melting-point of which (160°) was much lower than that of the active forms (181°) But it was recognized that this could not be a racemic compound because by repeated fractional crystallization it could be split up into antipodes[1] Possibly the same conditions will be disclosed by fuller investigations of other substances in group B. See § 32.

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[1] Fischer and Stahel Ber d chem. Ges., 24, 534. Fischer and Curtiss Ber d chem. Ges., 25, 1025

In those cases in which racemic bodies have about the sam melting-point as have the components, it is also probable tha they are merely physical mixtures The conditions the resemble those which Küster[1] found in isomorphous mixture where the melting-points lie between those of the constituent

Then again, a change in the melting-point has been foun in certain substances. Wallach observed[2] that the meltin point of racemic β-carvonepentabromide, which was abo 96°–98° at the start, and quite different from that of th components (86°–87°), becomes lower by repeated crysta lization of the preparation. It appears here that a parti decomposition of the racemic compound must have taken plac

Walden has called attention to the parallelism betwee specific gravity and melting-point of the optical modifications

A consideration of the above tables shows in fact, that wit those bodies in which the specific gravity of the racemic for is greater than that of the active components, the same relatio holds for the melting-points, and *vice versa*.

2. Liquid Racemic Compounds

25. On mixing equal amounts of the antipodes of liqu substances it may happen that immediate solidification to crystalline mass takes place, which is inactive in solution ; i such case a true racemic compound certainly is formed. Th occurs, for example, by pouring together of *d*- and *l*-caron oxime (v. Baeyer).[4]

If, on the other hand, the inactive mixture remains liqui it is uncertain whether it should be considered as a racem compound. There is evidently no ground for this, if it found that the physical properties of the mixture are t same as those of the components. This has been observe for example, with limonene, also with carvone, in respect specific gravity and boiling-point (Wallach),[5] conine, wi respect to specific gravity, boiling-point and solubility (Lade burg),[6] further with the esters of *l*- and inactive glyceric ac and diacetylglyceric acid Frankland and (MacGregor).[1] The agreement in the specific gravities of liquid inactive and active isomers, leads to the conclusion that the inactive forms must be considered as mechanical mixtures, as I. Traube has shown by the aid of his atomic constants and molecular covolume data.[2]

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[1] Kuster. Ztschr. phys Chem., **5**, 601, **8**, 577

[2] Wallach Ann. Chem (Liebig), **286**, 138

[3] Walden: Ber d chem Ges., **29**, 1704.

[4] v. Baeyer. *Ibid.*, **28**, 640.

[5] Wallach Ann. Chem. (Liebig), **286**, 138

[6] Ladenburg: *Ibid*, **247**, 81; Ber d. chem Ges., **28**, 163.

Such inactive mixtures may differ in chemical behavior, from their components. *d*- and also *l*-limonene are transformed by bromination into rhombic-hemihedral crystals of the tetrabromide, melting at 104°, while the mixture of the two isomers (dipentene) furnishes rhombic crystals melting at 124°, which are less soluble in ether than the first, and which form a racemic compound (dipentene tetrabromide) (Wallach).[3] The racemization probably begins here, however, with the formation of the crystalline compound, and the behavior noted gives no proof therefore that the dipentene is already a real combination of the antipodes

Elevation of the boiling-point could be taken as an indication of raceme formation, but this has not yet been observed in a single case with certainty, experiment showing always practical agreement in this factor Besides, even with true racemic compounds, the possibility is present of finding not their own boiling-point, but that of the components, because at the high temperature necessary, dissociation into the last may take place

The temperature changes observed on mixing active isomers have been employed to decide the question under discussion. In this regard, the following facts are to be considered·

If the two antipodes unite to form a real racemic compound, which immediately separates in crystalline form, the increase of temperature observed is due partly to the heat of formation and partly to change in the state of aggregation. This is, for example, the case when concentrated solutions of *d*- and *l*-tartaric acid (Pasteur), or *d*- and *l*-limonenetetrabromide in ether, are mixed[4] With the tartaric acid there is also the heat of hydration, in consequence of forming racemic acid, $C_4H_6O_6 + H_2O$.

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[1] Frankland and MacGregor · J Chem Soc, **63**, 511

[2] I Traube Ber d chem Ges., **29**, 1394

[3] Wallach Ann Chem. (Liebig), **286**, 138.

[4] Ladenburg Ber d chem Ges., **28**, 1994

If the two antipodes are themselves liquid substances, and if no solid racemic body separates on mixing them, then a change of temperature may be due: first, to the heat of solution or dilution, or, secondly, to the possible formation of a liquid racemic compound.

Regarding the heat of solution observed on pouring together two miscible liquids, this may be shown according to the nature of the substances, and the proportions even, in a decrease of temperature as well as by an increase. As investigations of Bussy and Buignet,[1] and also of Favre,[2] have disclosed, the heat effect bears no definite relation to change of density which takes place. Thus, alcohol and ether mixed with contraction, carbon disulphide and chloroform with expansion, but in both cases there is a decrease in temperature. If alcohol and chloroform be mixed in different proportions, there is always contraction, but in spite of this, reversed temperature changes may be found, as shown by the following example.

Mixing proportions	Temp. change
6 mols chloroform + 1 mol alcohol	− 2.5°
$1\frac{1}{3}$ mols chloroform + 1 mol alcohol	0.0
1 mol chloroform + 6 mols alcohol	+ 4.2°

In general, as late investigations of Ladenburg[3] have also shown, large changes in volume seem to correspond to large temperature changes. If the contraction or dilatation is very small, that is, if the specific gravity of the mixture is very nearly that of the mean calculated from the mixing proportions, a very small temperature change is in general noted as in the case of methyl and ethyl alcohol, isobutyl and isoamyl formate, xylene and toluene, and so on (Ladenburg). But, on the other hand, large temperature changes have been observed; thus, on mixing two volumes of ether with three volumes of carbon disulphide there is no change of volume but notwithstanding this, there is a fall of temperature of 3.6 (Bussy and Buignet), and this is the case with some very similar liquids, such as *d*- and *l*-conine, with which Ladenburg found a fall of temperature of 1.4°. But *d*- and *l*-limonene mix without appreciable change of temperature.[1]

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[1] Bussy and Buignet. Jahresbericht, 1864, 62 to 69. Ann. chim. phys., [4], 4, 5.

[2] Favre. Jahresbericht, 1864, 66. Compt. rend., 59, 783.

[3] Ladenburg. Ber. d. chem. Ges., 28, 1991.

[4] Ladenburg. *Ibid.*, 28, 164.

As the above relations show, the temperature changes accompanying mixing or solution are of such different kinds, that the heat effects in consequence of a real combination of the antipodes may be quite uncertain. Therefore, neither an increase nor decrease of temperature which may be observed on mixing two active isomers, may be taken as definitely indicating the existence of racemization.

Finally, it may be remarked, that it has been found impossible through cryoscopic measurements also to prove racemization in liquid inactive bodies. Thus, Frankland and Pickard[2] found the simple molecular weight for the inactive methyldibenzyl ester of glyceric acid dissolved in acetic acid, benzene, nitrobenzene or ethyl bromide.

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26. The following may be given as the principal results of all of the above comparisons of the properties of racemic compounds with those of the active modifications:

1. True racemic compounds are found only among crystallizable substances. They have always a different crystalline form, and often an amount of water of crystallization different from that of the active isomers. Further, they show, as a rule, deviations in respect to specific gravity, melting-point and solubility, but often in different directions.

2. Inactive crystalline masses may be sometimes simple aggregations or growths of mixed enantiomorphic active crystals.

3. The existence of liquid racemic compounds is improbable, and up to the present time has not been shown.

The question as to whether an inactive body is a racemic compound or racemic mixture is besides, in many cases, only of secondary importance. Both forms may be split up into optical antipodes in the same way, and in this we have all that is really important in the respective substances, that is, their distinction from inactive configuration isomers.

[1] Ladenburg: Ber. d. chem. Ges., 28, 1994.

[2] Frankland and Pickard: J. Chem. Soc., 69, 128.

C. Formation of Racemic Bodies

Racemic bodies may be produced in the following ways :

1 By direct combination of the active antipodes.

2. From one of the active forms by action of higher temperature

3. By the chemical transformation of asymmetric bodies into asymmetric derivatives.

4. By the conversion of inactive symmetric bodies into asymmetric compounds.

27. Production of Racemic Bodies by Combination of Equal Amounts of the Antipodes. Temperature of Transition.—Certain phenomena may appear here which belong in the class of chemical equilibrium reactions, the important characteristic of which is, that for them a definite temperature exists which, if passed in the one direction or in the other, leads to the transition of one system of bodies into another or the reversion of the latter into the former Thus, the breaking up of a racemic body into its antipodes is possible, or, on the other hand, the reproduction of the racemic from the antipodes The transition temperature has been determined in but two cases ·

First with sodium ammonium racemate and the two corresponding tartrates When Pasteur permitted a solution of racemic acid which was saturated, half with soda and half with ammonia, to evaporate spontaneously, he obtained separate crystals of the *d* and *l* double tartrate salt. But on repeating the experiment, it did not always succeed ; thus, Staedel[1] observed only the formation of the racemate Scacchi[2] first noticed that the kind of crystal which separates depends on the temperature at which the evaporation takes place, and Wyrouboff[3] then determined 28° as about the limiting temperature above which racemate, and below which, on the contrary, the tartrates, crystallize out. A complete explanation of the phenomenon was first given by van' t Hoff and Deventer,[4] when they showed that we have to deal with a process here which can also take place outside of solution. If a finely powdered mixture of equal parts of right and left sodium ammonium tartrate, $NaNH_4C_4H_4O_6 + 4H_2O$, be sealed in a tube and exposed to a temperature which is kept below 27°, it remains quite unchanged; but above 27° the formation of crystals of the racemate, $NaNH_4C_4H_4O_6 + H_2O$, sets in, water being liberated at the same time which partially liquefies the mass. On the other hand, if powdered sodium ammonium racemate be mixed with water below 27° in the proportion of $2(NaNH_4C_4H_4O_6 + H_2O)$ $6H_2O$, the semi-fluid mass which forms at first, solidifies after a time to a dry mixture of the two tartaric acid salts. Above 27° this does not happen. The two reactions may be expressed by the following equations in which $T = C_4H_4O_6$:

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[1] Staedel Ber d chem Ges, 11, 1752 (1878)

[2] Scacchi Rendiconti dell Accad di Napoli, 1865, 250

[3] Wyrouboff Bull Soc Chim, 45, 52 (1886) ; Compt rend, 102, 627

[4] Van' t Hoff and Deventer Ber d chem Ges, 19, 2148 (1886); Ztschr phys Chem, 1, 165

$$\begin{array}{ccc} \text{Stable below } 27^\circ & & \text{Stable above } 27^\circ \\ \left.\begin{array}{l} d\ NaNH_4T + 4H_2O \\ l\ NaNH_4T + 4H_2O \end{array}\right\} & = & \left\{\begin{array}{l} r\,[NaNH_4\ T + H_2O]_2 \\ 6H_2O \end{array}\right. \end{array}$$

The change of one salt into the other may be recognized by aid of a dilatometer, which is filled partly with a mixture of the two tartrates and partly with oil, the slow formation of the racemate between 26.7° and 27.7° is accompanied by a marked increase in volume

Further investigations of van't Hoff, Goldschmidt and Jorissen[1] showed that the sodium ammonium racemate $(NaNH_4C_4H_4O_6 + H_2O)$, when heated to about 35°, undergoes a further change as it breaks up into sodium racemate and ammonium racemate, according to the equation

$$2[NaNH_4T\,H_2O]_2 = [Na_2T]_2 + [(NH_4)_2T]_2 + 4H_2O.$$

Sodium ammonium racemate can exist in solution, therefore, only within the narrow temperature limits of 27° to 35°

Again, it can happen that the separation of the double racemate may fail when a mixture of *d*- and *l*-sodium ammonium tartrates is exposed to a temperature higher than 27°, for example, to 30°, and instead a separation of crystals follows, consisting of a mixture of sodium racemate and ammonium racemate as in the last case. This is especially true when crystals of the last named salts are added to the solution. The change may be represented in this way:

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[1] van't Hoff, Goldschmidt and Jorissen. Ztschr. phys. Chem., 17, 49.

$$\left.\begin{array}{l} d\ 2[\mathrm{NaNH_4}T + 4\mathrm{H_2O}] \\ l\ 2[\mathrm{NaNH_4}T + 4\mathrm{H_2O}] \end{array}\right\} = \left\{\begin{array}{l} [\mathrm{Na_2}T]_2 \\ [(\mathrm{NH_4})_2T]_2 \\ 16\mathrm{H_2O} \end{array}\right.$$

The methods by which the transition temperatures of 30° and 35° were established consisted in tensimetric observations and determinations of solubility

Analogous relations, according to experiments of van't Hoff, Goldschmidt and Jorissen,[1] have been found to exist in the case of the potassium sodium racemate $[\mathrm{KNaC_4H_4O_6} + 3\mathrm{H_2O}]_2$, described by Wyrouboff,[2] and *d*- and *l*-Rochelle salt, $\mathrm{KNaC_4H_4O_6} + 4\mathrm{H_2O}$. A solution formed from the racemate or from the two tartrates is found in the following conditions according to the temperature

1. Below about —6° *d*- and *l*-potassium sodium tartrate exist in solution together

2 From about —6° on the combination to potassium sodium racemate begins, and especially on an addition of small crystals of this salt

$$\left.\begin{array}{l} d\ \mathrm{KNa}T + 4\mathrm{H_2O} \\ l\ \mathrm{KNa}T + 4\mathrm{H_2O} \end{array}\right\} = \left\{\begin{array}{l} [\mathrm{KNa}T + 3\mathrm{H_2O}]_2 \\ 2\mathrm{H_2O} \end{array}\right.$$

3. The double racemate exists up to the temperature of 41°, from that point it decomposes into the sodium racemate, $[\mathrm{Na_2}T]_2$, and potassium racemate,, $[\mathrm{K_2}T + 2\mathrm{H_2O}]_2$ according to the equation

$$2[\mathrm{KNa}T + 3\mathrm{H_2O}]_2 = [\mathrm{Na_2}T]_2 + [\mathrm{K_2}T + 2\mathrm{H_2O}]_2 + 8\mathrm{H_2O}$$

4. If the formation of the potassium sodium racemate from the two tartrates fails, which may happen by excluding every trace of the first named salt, a conversion of the tartrates into potassium racemate and sodium racemate is possible. This takes place at a temperature of 33°.

$$\left.\begin{array}{l} d\ 2(\mathrm{KNa}T + 4\mathrm{H_2O}) \\ l\ 2(\mathrm{KNa}T + 4\mathrm{H_2O}) \end{array}\right\} = \left\{\begin{array}{l} [\mathrm{Na_2}T]_2 \\ [\mathrm{K_2}T + 2\mathrm{H_2O}]_2 \\ 12\mathrm{H_2O} \end{array}\right.$$

Therefore under varying conditions very different salts may crystallize from the solution.

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[1] van 't Hoff, Goldschmidt and Jorissen Ztschr phys Chem, 17, 505

[2] Wyrouboff Ann chim phys [6], 9, 224.

Exact knowledge of transition temperatures extends only to the two salts just described.

With a number of substances it has been observed that when mixed solutions of their antipodes are allowed to evaporate under ordinary conditions of temperature active crystals only, never racemic, are formed. Thus, Piutti[1] did not succeed in uniting *d*- and *l*-asparagine to form a racemic compound, while it was possible with *d*- and *l*-aspartic acid. As already remarked, according to Fisher and Curtiss,[2] the lactone of *d*- and *l*-gulonic acid separates in independent enantiomorphous crystals, while, on the other hand, a racemic calcium salt and phenylhydrazide may be obtained. It has likewise been found impossible to obtain by crystallization racemic forms of several other bodies, as the zinc ammonium salt of active lactic acid, glutaminic acid, glutaminic acid hydrochloride, homo-aspartic acid and camphoric acid In all of these cases it cannot be assumed that the antipodes do not possess the property of uniting to form a racemic body, knowledge of the transition temperatures simply is lacking

28. Production of Racemic Bodies from One of the Active Forms by Heat.—By long application of heat, many active substances suffer a gradual decrease in their rotating power, without undergoing a change in composition It was at first supposed that a destruction of the active property took place, but the phenomenon was later recognized as one of racemization. In consequence of the enlarged atomic motion by increase of temperature, a conversion into molecules of the opposite modifications follows until finally a condition of equilibrium is established, in which just as many molecules of the *d*-form are changed into the *l*-form as *vice versa*, that is, in which the mixture consists of equal amounts of the two antipodes. Van 't Hoff[3] has treated the question from the standpoint of thermodynamics.

The phenomenon was first observed by Pasteur[4] in the case of tartaric acid, when he heated *d*-cinchonine tartrate five or six hours to a temperature of 165° to 175° in an oil-bath The alkaloid was changed first, being converted mainly into cinchonicine, and then the production of racemic acid gradually followed, which was recovered by conversion into the calcium salt. *l*-Cinchonine tartrate behaves in a similar manner The alkaloid takes no part in the reaction, it only protects the tartaric acid from destruction by the heat. The formation of racemic acid follows also when dry tartaric acid is heated to 170° to 180°, and likewise, by boiling its aqueous or weak hydrochloric acid solution several days, which, however, brings about a conversion of only a few per cent.[1] Racemization follows almost completely on heating 30 grams of tartaric acid with 3 or 4 cubic centimeters of water for thirty hours to 175° (Jungfleisch)[2] Further, tartaric acid, in the form of its ethyl ester, is very easily changed by boiling into racemic acid (Pasteur).[3] The addition of several bodies aids the change; when tartaric acid is mixed with some aluminum tartrate and heated in an autoclave to 140° a conversion into racemic acid follows quickly, but some mesotartaric acid is produced at the same time (Jungfleisch)[4]

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[1] Piutti Ber d chem Ges, 19, 1694.

[2] Fischer and Curtiss Ber d chem. Ges., 25, 1025.

[3] van 't Hoff Lagerung der Atome im Raum, 2nd ed., p 33.

[4] Pasteur Compt rend., 37, 162 (1853)

Racemization by high and long heating in closed tubes has been observed in other substances, as

l-Aspartic Acid.—The transition takes place easily when an aqueous solution of the hydrochloric acid compound is heated some hours to 170° or 180° (Michael and Wing).[5]

d- and l-Mandelic Acid—Small amounts (3 or 4 grams) of the dry substance, thirty hours to 160° (Lewkowitsch).[6]

d- and l-Isopropylphenylglycolic Acid.—Heating for forty hours with water to 180° or 200° (Fileti).[7]

d-Camphoric Acid.—Heating with a little water to 170° or 180° (Jungfleisch,[8] Friedel)[9]

The active terpenes suffer a decrease in rotation when heated to about 250° to 300°, but show at the same time an elevation in the boiling-point and specific gravity, from which it follows that polymerization as well as racemization has taken place. *d*- as well as *l*-limonene and pinene are converted into dipentene, partly also into terpinene (Wallach).

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[1] Dessaignes Jahresbericht, (1856), 463, (1863), 301

[2] Jungfleisch Compt rend, **75**, 439, 1739

[3] Pasteur *Loc cit*

[4] Jungfleisch Compt rend, **85**, 805

[5] Michael and Wing Ber d chem. Ges, **17**, 2984

[6] Lewkowitsch *Ibid*, **16**, 2721

[7] Fileti Gazz chim ital, **22**, II, 395.

[8] Jungfleisch Jahresbericht, (1873), 631

[9] Friedel Compt rend, **108**, 978

The temperature of racemization is not in all cases as high as for the bodies given above. As Wallach[1] found, *d*- and *l*-limonene hydrochloride have the property of changing gradually even at the ordinary temperature. A preparation which was examined when produced, and after having been kept several weeks showed a decrease in rotation from $[\alpha]_D = +39.5°$ to 6.2°, which, as could be demonstrated, was due to the conversion into the dipentene compound. Besides, the boiling-point of the substance, which was originally 97.5°, increased to about 170° (under 11 mm.), which indicated polymerization at the same time.

In some cases it has been observed that racemization is hastened by addition of certain substances and is completed at a much lower temperature. As already mentioned tartaric acid in presence of aluminum tartrate is easily converted into racemic acid. Active amyl alcohol when heated alone must be maintained a long time at 250° to 300° to lose its rotating power, but on treatment with sodium or with caustic potash the change is much more rapid, from the inactive product obtained dextroamyl alcohol could be separated by aid of fungi (Le Bel).[2] On repeating this experiment Borucki[3] found that when amyl alcohol was heated with potash in an autoclave during ten hours to 160° the angle of rotation, α_D for 1 dm., decreased from 1.01° to 0.10°, and that by heating under ordinary pressure with renewed alkali, complete inactivity resulted only after 465 hours. According to Walden[4] almost perfect inactivity may be reached much more rapidly by dissolving one-tenth its weight of sodium in the amyl alcohol and heating then 3½ hours to 200° or 220° in an autoclave. Erlenmeyer and Hell[5] have observed that by treating *d*-valeric acid from fermentation amyl alcohol with a few drops of stror sulphuric acid and heating then ¼ hour in a sealed tube 250° complete inactivity resulted Whether this was due racemic formation or not was not established. Active leuci which is not changed by heating with water to 170°–180° converted by addition of baryta water at 150°–160° into the compound (Schulze and Bosshard)[1] The racemization terpenes is hastened by addition of sulphuric acid, either co centrated or diluted with alcohol (Wallach).[2]

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[1] Wallach. Ann. Chem. (Liebig), 270, 190.

[2] Le Bel. Bull. Soc. Chim., [2], 25, 545.

[3] Borucki. Inaug. Diss., Berlin, 1866, Centrbl., 1887, p. 580.

[4] Walden: Ztschr. phys. Chem., 17, 711.

[5] Erlenmeyer and Hell. Ann. Chem. (Liebig), 160, 302.

29. Racemization by Conversion of Asymmetric Bodies in Asymmetric Derivatives.—If an active molecule retains its co stitution in a chemical change, that is, for example, if a chan of an acid into ester, salt or amide, or of an alkaloid into combination with an acid is concerned, the activity is alwa retained This is the case also with simple transitions, as active amyl alcohol into valeric acid, camphor into campho acid, asparagine into aspartic acid and maleic acid, amygdal into amygdalic or mandelic acid, etc.

But under certain conditions the product may be inacti This is particularly the case in the production of derivativ in which the atoms directly united to the asymmetric carb take a part in the reaction. If, for example, in active mal acid, $CO_2H—{}^*CH.OH—CH_2—CO_2H$, the hydroxyl group combination with the *C be replaced by Br by aid of hydr bromic acid, racemic bromsuccinic acid, $CO_2H—{}^*CH.Br-CH_2—CO_2H$, results (Kekulé).[3] Further, *l*-valeric aci $(C_2H_5)—{}^*CH—(CH_3)(CO_2H)$, is converted completely in racemic bromvaleric acid, $(C_2H_5)—{}^*CBr—(CH_3)(CO_2H)$, treatment with bromine and phosphorus at a low temperatu followed by heating to 100° (Schütz and Marckwald).[4] Th same active valeric acid when oxidized in aqueous solution potassium permanganate yields racemic oxyvaleric aci $(C_2H_5).{}^*COH.(CH_3)(CO_2H)$.

In changes like the above, by keeping the temperatures low as possible, the racemization may be often prevented a an active derivative obtained. Walden[1] succeeded in converting malic acid into dextromonochlorsuccinic acid by the action of phosphorus pentachloride with addition of chloroform which prevented the temperature from exceeding 62°. By the same process[2] (PCl_5 or PBr_5 and $CHCl_3$) he converted a number of hydroxy acids or their esters directly into active halogen derivatives, as, for example, *l*-dimethyl and diethyl malate into dextrobromsuccinic esters, *d*-diethyl tartrate into *l*-ethyl monobrommalate; *l*-ethyl and propyl mandelates into dextrophenylchloracetic esters; *l*-mandelic acid into *d*-phenylchloracetyl chloride, $C_6H_5.CHCl.COCl$ (by heating with PCl_5 to 160° under a return condenser without addition of chloroform); *l*-calcium lactate (without chloroform) into *d*-chlorpropionyl chloride, CH_3 CHCl COCl

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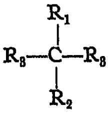
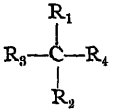
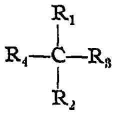
[1] Schulze and Bosshard· Ztschr. physiol. Chem , **10**, 135.

[2] Wallach Ann Chem (Liebig), **227**, 283, **239**, 11

[3] Kekulé: *Ibid*, **130**, 25

[4] Schütz and Marckwald: Ber d. chem Ges., **29**, 58.

The same reactions which bring about racemization when taking place at the *C permit the formation of active derivatives from active substances when the *C remains untouched If the substance contains several *C atoms, at least one of them must be excluded from the reaction if active derivatives are to be secured From borneol, $C_{10}H_{17}$ OH, active bornyl chloride, $C_{10}H_{17}Cl$, is produced by action of HCl or PCl_5 (Kachler).[3] Camphor furnished by action of bromine active bromcamphor, $C_{10}H_{15}BrO$ (Montgolfier).[4] In the oxidation of active substances with permanganate, active oxidation products result in many cases; thus, chitenine, $C_{19}H_{22}N_2O_4$, from quinine, $C_{20}H_{24}N_2O_2$ (Skraup),[5] chincotenine, $C_{18}H_{20}N_2O_3$, from cinchonine, $C_{19}H_{22}N_2O$ (Hesse).[6]

30. Production of Racemic Compounds by Conversion of Symmetric Bodies into Asymmetric.—If a symmetric compound,  $R_3—\overset{\overset{\large R_1}{|}}{\underset{\underset{\large R_2}{|}}{C}}—R_3$, in consequence of the substitution of one of the two radicals R_3 R_3 by R_4 be converted into an asymmetric compound, the formation of both  $R_3\!-\!\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{C}}\!-\!R_4$ and  $R_4\!-\!\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{C}}\!-\!R_3$ is possible. On account of the symmetry of the original molecule there is no reason why one of these antipodes only should be formed, on the contrary, the production of both with equal rapidity should take place, and the resulting product would be racemic The correctness of this view has been shown by experience, as it has been possible to prove that the inactivity of all asymmetric bodies which have not been made from active ones, depends in reality on the production of racemic forms While it is true that not all of these inactive products have been split up into their antipodes, enough such reactions have been carried out to show the generality of the rule

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[1] Walden : Ber d. chem Ges , **26**, 210

[2] Walden · *Ibid* , **28**, 1287

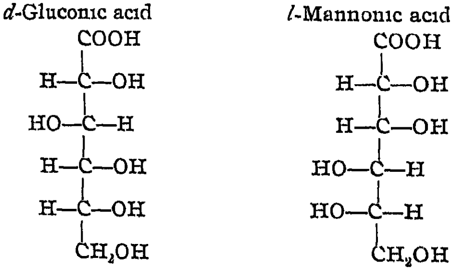
[3] Kachler Ann Chem (Liebig), **197**, 93

[4] Montgolfier · Ann chim phys., [5], **14**, 140.

[5] Skraup : Ann. Chem. (Liebig), **199**, 344

[6] Hesse, *Ibid.*, **176**, 233.

31. **Racemic Compounds from Right- and Left-Rotating Isomers of Different Configurations.**—Such bodies, which should be active, have not yet been produced Liebermann[1] obtained, by evaporating an ethereal solution of equal weights of *d*-cinnamic acid dibromide ($[\alpha]_D = +64°$) and *l*-allocinnamic acid dibromide ($[\alpha]_D = -70°$), a residue which on treatment with carbon disulphide could be separated into the components E Fischer[2] has attempted to combine compounds with each other whose configurations present only partially the object-reflection relation, as is the case with



From a mixture of equal parts of the two acids which was evaporated to a sirup, pure *l*-mannonic acid lactone only separated, and from a mixture of the calcium salts, *d*-calcium gluconate crystallized first.

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[1] Liebermann Ber d chem Ges, **27**, 2045

[2] Fischer. *Ibid*, **27**, 3226

The oppositely rotating forms of camphoric acid and isocamphoric acid do not unite to yield a racemic compound (Aschan).[1]

A tendency, therefore, toward the formation of such half-racemic bodies does not appear to exist.

D. Resolution of Racemic Bodies

For the decomposition of racemic bodies into the antipodes, we have as yet three methods, which were all discovered by Pasteur, and first applied to racemic acid. These are

1 Resolution by crystallization.
2. Resolution by aid of active compounds
3. Resolution by aid of fungi

The principles underlying these methods have been explained already and it remains to discuss in this chapter the practical methods of carrying out the processes

1. Resolution by Crystallization. Spontaneous Resolution

32. This process depends on the facts that racemic compounds in solution, under proper temperature conditions, break up into their antipodes and that these last may be separated by evaporation of the solution in the state of enantiomorphic crystals which may be sorted out by aid of the characteristic planes into active right and left forms Equal amounts of the two antipodes are obtained The transition temperatures explained in § 27 must be considered as these are different for different substances

The method was first applied by Pasteur[2] in 1848 for the splitting of racemic acid in the form of sodium-ammonium salt and may be best carried out in the following manner:[3] An aqueous solution of racemic acid is divided into two parts, one being saturated with sodium carbonate or hydroxide and the other with ammonia in excess. The mixture is then evapo-

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[1] Aschan Ber d chem Ges, 27, 2001.
[2] Pasteur Ann chim phys [3], 24, 442 (1848)
[3] Pasteur *Ibid*, 28, 56 (1850).

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rated on the water-bath until crystallization begins on cooling. The crystals are redissolved by the aid of water and a little ammonia after which the solution is allowed to stand in a wide crystallizing dish for spontaneous evaporation As explained in § 27 the temperature must be kept below 27°. It is advisable to remove a part of the crystals each morning, because, in consequence of the rise of temperature during the day, partial solution might follow with loss of the hemihedral faces. As the solution gradually loses ammonia a little must be added from time to time, sufficient to maintain a weak alkaline reaction The separated crystals which are illustrated in Figs. 4 and 5, and which often reach a length of several centimeters, are removed from time to time by the aid of pincers and sorted out after examination with a magnifying glass. If the individual crystals have grown together or are united into groups it is best to bring them into solution by adding a little water and warming and then repeat the whole crystallization. The separation of the *d*- and *l*-sodium ammonium tartrate is facilitated by placing the two kinds of crystals in the evaporated liquid at the start and as far apart as possible

Very often the crystallographic examination is difficult because the hemihedral faces are but imperfectly developed, o cannot be found at all In such a case the question as t whether a crystal consists of the right or left tartrate or o the racemate may be decided by a procedure suggested b Anschütz[1] which depends on this that the calcium racemate i much less soluble than the two calcium tartrates. The mothe liquor is separated from the crystals by washing with a littl water, a fragment is dissolved in a small volume of water an the solution is divided into two parts. One part is mixed wit about 3 cc. of a saturated solution of dextro-calcium tartrat and allowed to stand some time, if a precipitate appears i shows the presence of the left tartrate. If a precipitate doe not form and if the other half of the liquid gives a precipitat with a solution of levo-calcium tartrate the presence of th right tartrate is indicated. Finally, if precipitation takes plac in both cases, racemic acid is shown to be present in the crysta

As Pasteur[2] found, the *d*- and *l*-tartrates separate always i exactly equal amounts at any point in the crystallization, for if at any time the whole mass of crystals be removed and dissolved in water the solution will be found to have no rotating power, and the mother-liquor likewise not. The two salts must therefore possess exactly the same solubility. Jungfleisch, on the contrary, believes[1] that the right salt is less soluble than the left, inasmuch as he found more of the first in the early part of the crystallization, and more of the second in the last part

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[1] Anschutz Ann Chem (Liebig), **226**, 193

[2] Pasteur Ann chim phys [3], **24**, 458

The separation of the two tartrates may be accomplished as Gernez[2] found, in this way· The original solution prepared by heat is carefully kept free from crystals of the salt or from dust and allowed to cool down until it reaches the supersaturated condition, when a few crystals of the *d*- or *l*-sodium ammonium tartrate are thrown in Then the separation of the corresponding salt follows, while the other remains in solution

Besides racemic acid the following racemic bodies have been resolved by crystallization

r-Fermentation lactic acid, in the form of its zinc-ammonium salt, $ZnNH_4(C_3H_5O_3)_3 + 3H_2O$, which breaks down into the *d*- and *l*- lactates, $ZnNH_4(C_3H_5O_3)_3 + 2H_2O$ (Purdie)[3] This takes place when to a concentrated solution of the racemic compound, brought to supersaturation by cooling, crystal fragments of one of the lactates are added, which brings about a separation of the corresponding salt. The crystal fragments needed for this are prepared by splitting the *r*-lactic acid by means of the more easily performed strychnine method If the solution of the *r*-zinc-ammonium salt alone be allowed to crystallize spontaneously at the ordinary temperature most of the salt separates as such.

Solutions of the following four compounds furnish simultaneously crystals of the *d*- and *l*-modifications, which can be distinguished crystallographically, when their aqueous solutions are allowed to evaporate at the ordinary temperature.

dl-Gulonic acid lactone, formed by mixing the antipodes (Fischer and Curtiss).[4] Racemic crystals are not formed.

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[1] Jungfleisch· Bull. Soc. Chim [2], 41, 226

[2] Gernez, Compt. rend , 63, 843

[3] Purdie, J Chem Soc , 63, 1144 to 1151

[4] Fischer and Curtis: Ber. d. chem. Ges , 25, 1046

dl-Asparagine by action of ammonia on esters of maleic and fumaric acid (Körner and Menozzi),[1] or from the antipodes (Piutti).[2] Racemic crystals are not formed under the same conditions

r-Homoaspartic acid, formed by the action of alcoholic ammonia on the ethyl esters of citra-, mesa- and itaconic acids (Körner and Menozzi).[3]

r-Glutaminic acid from *r*-glutamide (Menozzi and Appiani).[4] The holohedric crystals of the *r*-acid on repeated crystallization from water yield crystals with right- and left-hemihedral surfaces.

2. Resolution by Active Compounds

33. This method is based, as explained in § 18, on the unequal solubilities shown by the salts of a *d*- and *l*-acid with the same active base (alkaloid), or of a *d*- or *l*-base with the same acid (*e.g* tartaric acid) It was first applied by Pasteur[5] in the decomposition of racemic acid, by which he found that when a hot aqueous solution of the acid was mixed with molecular proportions of different cinchona bases to saturation there separated on cooling, not the racemic acid, but the tartaric acid salt; with quinine or quinicine the first crystallization contained *d*-tartaric acid, but *l*-tartaric acid, on the contrary, with cinchonine or cinchonicine Later the method was applied to the resolution of many other racemic acids, and of these, first to malic acid by Bremer[6] in 1880. Then it was used with bases, and first with synthetic conine whose resolution was carried out by Ladenburg[7] in 1886 by means of *d*-tartaric acid. The process, which has already rendered good service in many instances, aids especially in the separation of the component in the less soluble salt in pure condition, while on the other hand, the purification of the component remaining in the mother-liquor offers, frequently, considerable difficulty, as it cannot be easily separated from the first. But in

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[1] Korner and Menozzi Ber d chem Ges, **21**, Ref 87

[2] Piutti: *Ibid*, **19**, 1694.

[3] Korner and Menozzi · *Ibid.*, **27**, Ref 121

[4] Menozzi and Appiani. *Ibid*, **24**, Ref 399, **27**, Ref 121

[5] Pasteur Compt. rend, **36**, 197; **37**, 162, Ann chim phys [3], **38**, 437

[6] Bremer Ber. d chem Ges, **13**, 352

[7] Ladenburg *Ibid.*, **19**, 2582

most cases, it is a question of securing one of the antipodes only, the second being obtainable in some other way.

a. Resolution of Racemic Acids by Aid of Alkaloid

As remarked in §18, the alkaloids exhibit no regular behavior with respect to which one of the optical modifications of an acid they unite with, to form the less soluble salt; the same base precipitates the *d*-salt of one acid, and the *l*-salt of another. But in the case of the cinchona bases, the rule appears to obtain, that if those of the formula $C_{19}H_{22}N_2O$ (cinchonine, cinchonidine, cinchonicine) precipitate the *l*-modification, then those of the formula $C_{20}H_{24}N_2O_2$ (quinine, quinicine, quinidine) yield the less soluble salt with the *d*-modification. In general, by preliminary tests, it is necessary to find the most suitable alkaloid, that is, the one which yields well crystallizable salts with the acid in question.

At present, in the splitting of the acids, the following alkaloids, which are all monacid bases, are most commonly employed.

Cinchonine.—Crystallized: $C_{19}H_{22}N_2O = 294$. Dextrorotatory. Difficultly soluble in cold or warm water. Soluble at 20° in 126 parts of alcohol of 84 per cent by volume.

Cinchonidine.—Crystallized: $C_{19}H_{22}N_2O = 294$. Levorotatory. At 10° soluble in 1680 parts of water or in 19.7 parts of 80 per cent alcohol by volume.

Quinine.—Crystallized: $C_{20}H_{24}N_2O_2 + 3H_2O = 378$. Levorotatory, soluble in 773 parts of boiling water and in 1.13 parts of absolute alcohol at 20°.

Quinidine.—Crystallized: $C_{20}H_{24}N_2O_2 + 2\frac{1}{2} H_2O = 369$. Effloresced $C_{20}H_{24}N_2O_2 + 2H_2O = 360$. Dextrorotatory. Soluble in 750 parts of boiling water and in 26 parts of 80 volume per cent. alcohol at 20°.

Strychnine.—Crystallized: $C_{21}H_{22}N_2O_2 = 334$. Levorotatory. Soluble in 2,500 parts of boiling water. Insoluble in absolute alcohol. Soluble in 120 parts of cold or in 10 parts of boiling alcohol of 80 volume per cent.

Brucine.—Crystallized: $C_{23}H_{26}N_2O_4 + 4H_2O = 446$. Levorotatory. Soluble in 150 parts of boiling water, easily soluble in alcohol.

Morphine.—Crystallized: $C_{17}H_{19}NO_3 + H_2O = 303$. Levo-rotatory. Difficultly soluble in cold, readily soluble in hot water Soluble in 40 parts of cold or in 30 parts of boiling absolute alcohol

The alkaloids and racemic acids, the latter taken with the simple molecular weight, have been usually combined in the molecular proportions of 1.1 With the monobasic acids the neutral salts are formed, and with the dibasic acids, acid salts, which have the advantage of easier crystallization. In some cases (as racemic acid, cinnamic acid dibromide) it has been found advantageous to take 2 molecules of acid to 1 of the base, which leaves half of the acid and in form of one of the antipodes, mainly in uncombined condition.

The crystallization of the less soluble salt and its separation from the more soluble one, is accomplished in several ways, depending on the nature of the substances. (1) By cooling the hot saturated solution; (2) By slow evaporation of the solution at the ordinary temperature and fractional crystallization; (3) By adding a crystal of the less soluble salt to the strongly concentrated or supersaturated solution (sowing, inoculation) It has been found here, that crystals may be used, which do not contain the modification of the acid to be separated, but the one with opposite rotation. For example, the addition of a crystal of *l*-cinchonine malate to a solution of racemic cinchonine malate causes a separation of the *d*-salt, a phenomenon which Bremer[1] has explained from the observations of Groth[2] on quartz, sodium chlorate, and sodium periodate, to depend on the tendency shown by enantiomorphous crystals to form twins consisting of the oppositely rotating varieties.

Below is given a résumé of the racemic acids which have been split by the aid of alkaloids, along with a discussion of the most important observations made in the experiments.

Racemic acid, as is well known, was first broken up by Pasteur with initial separation of:

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[1] Bremer Ber d chem Ges, 13, 352.

[2] Groth Pogg Ann, 158, 214

	Proportions used. Base		Acid
a The *l*-tartrate			
By cinchonine from alcoholic solution[1]	1	:	1
cinchonicine from aqueous solution[2]	1	:	1
b The *d*-tartrate			
By quinine from alcoholic solution[1] . ..	1	:	1
quinicine from aqueous solution[2]	1	:	1
brucine from alcoholic solution[1]	1 2	: :	1 1

For the separation of the *l*-acid, which is always the desired product, cinchonine serves best and may be used with advantage in the manner suggested by Marckwald[3] in which for 2 mols of $C_4H_6O_6 = 300$. 1 mol of $C_{19}H_{22}N_2O = 294$, that is about equal weights of each, is taken To the boiling aqueous solution of the racemic acid the cinchonine is added in small portions, and enough water then to maintain a clear solution. On cooling *l*-cinchonine tartrate crystallizes out, and after standing a day, may be filtered off The yield is about two-thirds of the theoretical After a second crystallization from hot water the salt is decomposed by ammonia, and from the solution separated from the cinchonine by filtration the *l*-tartaric acid is thrown down by lead acetate The lead salt is decomposed by hydrogen sulphide, or with larger amount, better by dilute sulphuric acid for recovery of the free acid From the mother-liquor of the *l*-cinchonine tartrate, which contains mainly the free *d*-acid along with small amounts of the *l*-acid and the cinchonine salts of both, crystals of acid *d*-cinchonine tartrate separate after a time and can be worked up for recovery of the base The liquid filtered from these is divided into two halves, one of which is exactly saturated with soda and the other with ammonia, and after filtration of the separated cinchonine, these are united and concentrated by evaporation. After cooling *d*-sodium ammonium tartrate crystallizes first. The mother-liquor is then allowed to evaporate until a portion tested in the polariscope is found to be inactive or slightly levorotatory. The racemate is now present which can be converted into free acid and treated anew with cinchonine.

[1] Pasteur. Ann. chim. phys., [3], 38, 437.
[2] Pasteur: Compt rend., 37, 162
[3] Marckwald. Ber. d chem. Ges., 29, 42.

Malic acid.—The *r*-acid obtained by reduction of racemic acid by means of hydriodic acid, was converted by Bremer[1] into the acid cinchonine salt, and to the concentrated solution a crystal of the acid cinchonine salt of common malic acid from mountain-ash berries was added. Crystallization followed, and after conversion into acid ammonium malate furnished this salt in the right-hand modification. As the corresponding salt of ordinary malic acid is levorotating in all concentrations,[2] this shows the production of the antipode. From the mother-liquor of the *d*-cinchonine malate, the ordinary *l*-acid ammonium malate could be obtained, but not in pure condition.

Methoxysuccinic acid, $CO_2H—CH(O.CH_3)—CH_2—CO_2H$ — *a*, with *cinchonine*, 1 : 1, in aqueous solution evaporated over sulphuric acids yields first crystals of the acid *d*-salt, and from the mother-liquor, the *l*-salt. Both antipodes are obtained pure (Purdie, Marshall and Bolam).[3]

b, with *strychnine*, 1 : 1 in water. The *l*-salt is somewhat less soluble. The concentrated supersaturated solution was treated with a crystal of the *l*-salt, which caused separations of the corresponding compounds. Both antipodes were obtained pure (Purdie and Bolam).[4]

Ethoxysuccinic acid with *cinchonidine*, 1 : 1. Crystals of the *d*-salt separate first on cooling the hot aqueous solution (Purdie and Walker).[5]

Isopropoxysuccinic acid with *strychnine*. With the base and acid in proportion, 2 : 1, the neutral *l*-salt crystallizes first, and then the *d*-salt. With 1 : 1 the acid *l*-salt separates first, while the *d*-salt forms an uncrystallizable sirup, which can be brought to crystallization by conversion into the neutral salt. Both antipodes are pure (Purdie and Bolam).[6]

Pyrotartaric acid with *strychnine*, 1 : 1. By evaporation of the aqueous solution, the *d*-salt separates first. By repeated crystallization, separation of the acid and reconversion into the strychnine salt, the *d*-acid was obtained in pure condition, but not the *l*-acid (Ladenburg).[1]

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[1] Bremer: Ber. d. chem. Ges., **13**, 351.

[2] See Schneider: Ann. Chem. (Liebig), **207**, 274.

[3] Purdie and Marshall: J. Chem. Soc., **63**, 217; Purdie and Bolam: *Ibid.*, **67**, 944.

[4] Purdie and Bolam: *Ibid.*, **67**, 946.

[5] Purdie and Walker: *Ibid.*, **63**, 236.

[6] Purdie and Bolam: *Ibid.*, **67**, 952.

Lactic acid with *strychnine*, 1 : 1. The aqueous solution subjected to fractional crystallization gave, at first, products which on conversion into the ammonium or zinc salt yielded these in the right-rotating form, that is, they contained the *l*-acid. From the last crystallizations, the *d*-acid (salts, levorotatory) was obtained By repeated crystallization of the strychnine salts, both antipodes were obtained pure (Purdie and Walker).[2]

α-Oxybutyric acid, $CH_3.CH_2$ $CHOH.CO_2H$, with *brucine* The salt of the *l*-acid crystallizes first (Guye and Jordon)[3]

Valeric acid, $CH_3—CH_2—{}^*CH.CH_3—CO_2H$, (from ethylmethyl malonic acid) with *brucine* 1 1 On cooling the solution prepared by the aid of heat, the *l*-salt separates first. By oft-repeated recrystallization of the less soluble fractions, (*l*-salt) the rotation of the liberated acid was brought up to a maximum ($[\alpha]_D = -17\ 85^\circ$) The *d*-acid could not be obtained in the same strength The reason for the difficult separation is found in the fact, that *d*-, *l*-, and *r*-brucine valerate are isomorphous with each other The crystals are monoclinic hemimorphous (Schutz and Marckwald).[4]

Galactonic acid with *strychnine.*—The lactone of the *r*-acid is dissolved in 70 per cent alcohol and boiled with an excess of finely powdered strychnine. The filtrate is evaporated after addition of water, which throws out part of the base, to the condition of a thin sirup On cooling, fine needles crystallize which consist largely of the *d*-salt, the same is true of the second crystallization The mother-liquor contains the *l*-salt Both antipodes are secured by repeated recrystallizations of the strychnine salts. The lactone of the *d*-acid rotates strongly to the left, that of the *l*-acid to the right (Fischer).[5]

Mannonic acid with *morphine* —From the solution obtained by boiling the *r*-acid with morphine the *d*-salt, after evaporating to a sirup, is separated in the form of crystals which are freed from mother-liquor by washing with methyl alcohc The *d*-salt only may be obtained pure (Fischer).[1]

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[1] Ladenburg · Ber. d chem. Ges , **28**, 1170

[2] Purdie and Walker J Chem. Soc , **61**, 757

[3] Guye and Jordon : Compt rend , **120**, 562.

[4] Schütz and Marckwald Ber. d. chem Ges , **29**, 52

[5] E. Fischer *Ibid.*, **25**, 1256

Mandelic acid with *cinchonine*, 1 : 1. This is dissolved boiling water, and after cooling a crystal of the *d*-salt is adde and the liquid allowed to evaporate. The yield of the *d*-sa is about 80 per cent. of the theoretical. After evaporati and long standing, the mother-liquor deposits crystals of tl *l*-salt. The *d*-acid may be obtained pure, but the *l*-acid best made from the amygdalin (Lewkowitsch).[2]

Tropic acid, $C_6H_5.{}^*CH.CH_2OH.CO_2H$, with *quinine* 1 . If the base, dissolved in dilute alcohol, be added to a h aqueous solution of the acid, and the mixture evaporated 100°, to beginning crystallization, the *d*-salt separates in pı white crystals. The mother-liquor on further concentrati leaves an oil which gradually solidifies to glassy crystals the *l*-salt. Both salts may be purified by recrystallizatic For the *d*-acid, $[\alpha]_D = + 71°$; the *l*-acid could not be obtain pure (Ladenburg and Hundt).[3]

Phenyl-αβ-dibrompropionic acid (cinnamic acid dibromid $C_6H_5\,{}^*CHBr\,{}^*CHBr.CO_2H$ From the *r*-compound the foll ing difficultly soluble salts were separated:

With	cinchonine,	1 base	: 2 acid,	from	alcohol	solution	the	*l*-aci
"	cinchonidine,	1 "	: 1 "	"	benzene	"	"	*l*-aci
"	quinidine,	1 "	: 1 "	"	alcohol	"	"	*d*-aci
"	strychnine,	1 "	: 1 "	"	"	"	"	*l*-aci
"	strychnine,	1 "	. 2 "	"	"	"	"	*d*-aci
"	brucine,	1 "	· 2 "	"	"	"	"	*d*-aci

With strychnine and 2 molecules of acid the neutral s $C_{21}H_{22}N_2O_2.C_9H_8Br_2O_2$, is always precipitated.

The separation of the pure antipodes which was undertal by Liebermann[8] by the strychnine method is difficult. It is t to proceed in this way: Dissolve 20 grams (2 mols) of cinnamic acid dibromide in 400 cc. of absolute alcohol and then 11 grams (1 mol) of strychnine as follows: Dissolve the alkaloid by aid of heat in an excess of hydrochloric acid and while still hot add excess of ammonia, which yields a crystalline easily filtered precipitate. This is washed with a little water and alcohol, and then, after puncturing the filter-paper, is washed into the cinnamic acid solution by the aid of 220 cc of absolute alcohol. After solution is effected by aid of heat, the mixture is allowed to stand about twenty hours, in which time 20 to 25 per cent. of the acid separates as strychnine salt of the *d*-form. (With 1 molecule of base to 1 of acid the *l*-form separates first.) For separation of the free acid the salt is suspended in water, acidified with hydrochloric acid and shaken with ether, and the ethereal solution, after a second shaking with water, evaporated. The highest observed rotation amounts to $[\alpha]_D = +68.3$ for 12 to 15 per cent. solution in alcohol. From the mother-liquor, after a second treatment with strychnine (1 of base : 2 of acid), more of the *d*-salt and then the salt of the *l*-acid may be obtained. The latter acid has been secured, however, with rotation up to $[\alpha]_D = -45.8°$ only.

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[1] Fischer: Ber d. chem. Ges., **23**, 379.

[2] Lewkowitsch · *Ibid.*, **16**, 1573.

[3] Ladenburg and Hundt· *Ibid*, **22**, 2590.

[4] Erlenmeyer, Jr.: *Ibid*, **26**, 1659; Hirsch: *Ibid.*, **27**, 887.

[5] Hirsch *Ibid*, **27**, 888.

[6] L Meyer, Jr. *Ibid.*, **28**, 3121; Liebermann: *Ibid.*, **26**, 247.

[7] Hirsch· *Ibid.*, **27**, 887.

[8] Liebermann: *Ibid.*, **26**, 247 and 829

Allocinnamic acid dibromide could be separated by aid of *cinchonidine* in benzene solution from which the salt of the *l*-acid crystallized. The highest observed polarization of the acid was $[\alpha]_D = -83.2°$. The *d*-acid could not be obtained pure (Liebermann[1]).

Phenyl-α β-dichlorpropionic acid, (cinnamic acid dichloride) with *strychnine.* 1 molecule of base, (40 grams) and 1 molecule of acid (45 grams), dissolved in 500 cc of 99.5 per cent. alcohol gave crystals of the *d*-salt after standing 40 hours. By separating the acid from the crystals, and treating again with strychnine, the *d*-acid was directly secured with maximum rotation. The mother-liquors from the first separation, after four treatments with strychnine, furnished the pure *l*-acid (Liebermann and Finkenbeiner).[2]

Phenyldibrombutyric acid (phenylisocrotonic acid dibromide), $C_6H_5.{}^*CHBr.{}^*CHBr.CH_2.CO_2H$, with *brucine,* 1 . 1. From the alcoholic solution, the *d*-salt separates on standing, the crystallization being induced by rubbing with a glass ro The yield is about three-fourths of the theoretical. B extracting the salt with enough hot alcohol to leave abo one-third undissolved, it may be obtained in quite pu condition. On evaporating the mother-liquor to dryness, tl *l*-salt separates, partly crystalline. With the proporti of 1 molecule of base to 2 of acid, a small amount of tl *d*-salt separates, but in purer form (L Meyer and Stein).[1]

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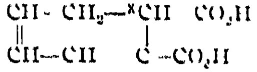
[1] Liebermann, Ber. d. chem. Ges., 27, 2041.

[2] Lieberman and Finkbeiner, Ber. d. chem. Ges., 26, 883; 27, 889.

Phenyl-α-bromlactic acid, $C_6H_5.{}^*CHOH.{}^*CHBr.CO_2H$ + H with *cinchonine.* The *d*-salt crystallizes in white needles fro the solution in absolute alcohol; the much more solul *l*-salt is obtained as a sirup which finally solidifies to a hor mass (Erlenmeyer, Jr).[2]

Isopropylphenylglycolic acid, $C_6H_4.C_3H_7.{}^*CHOH.CO_2H$, wi *quinine* and *cinchonine.* If one molecule of quinine and one the acid be dissolved in hot alcohol, and then treated with l water, and allowed to cool, the *l*-quinine salt separates T acid is liberated from the mother-liquor and combined in l aqueous solution with cinchonine. On cooling, the cinchoni salt of the *d*-acid separates first (Fileti).[3]

Dihydro-o-phthalic acid,



$$\begin{array}{llll} CH- & CH_2- & {}^*CH & CO_2H \\ \| & & | & \\ CH- & CH & C- & CO_2H \end{array}$$

, with *str* *nine*, 1 : 1 In fractional crystallization, the *d* salt separa first from aqueous solution (Proost).[4]

b *Resolution of Racemic Bases by Tartaric Acid.*

This method, first applied by Ladenburg[5] for the break up of synthetic coniine, has been carried out by convert the racemic base by treatment with ordinary *d*-tartaric a into a mixture of the bitartrates of the *d*- and *l*-bases separating these by fractional crystallization. In this wa was possible to obtain more or less readily that modification pure form which was contained in the less soluble salt, wh on the contrary, the other was always obtained in a condit with much lower rotation. In order to obtain the latter in a pure state, Marckwald[1] suggested that the mother-liquors from the precipitation with *d*-tartaric acid be decomposed with separation of the base and that this by addition of *l*-tartaric acid be converted into the *l*-bitartrate, which salt is now the more readily crystallizable. In this way the separation of the antipodes is complete. Other active acids than tartaric have not been tried as yet.

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[1] L. Meyer and Stein: Ber. d. chem. Ges., 27, 890.

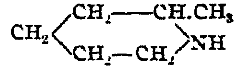
[2] Erlenmeyer, Jr.: Ann. Chem. (Liebig), 271, 159; Ber. d. chem. Ges, 24, 283

[3] Fileti; Gazz. chim. ital., 22, II, 395; Ber. d. chem. Ges., 26, Ref. 89

[4] Proost; Ber. d. chem. Ges., 27, 3185.

[5] Ladenburg. *Ibid.*, 19, 2582

The following racemic bases have been split.

α-Pipecoline, 
$CH_2\langle\begin{matrix}CH_2\text{—}CH.CH_3\\CH_2\text{—}CH_2\end{matrix}\rangle NH$
By saturation of the racemic base with one molecule of tartaric acid in aqueous solution, evaporation to a sirup and addition of a minute crystal of *d*-conine-*d*-bitartrate Ladenburg[2] obtained the salt of the *d*-base as a white tallow-like mass, while the *l*-base remained in the liquid pressed out. After repeated crystallization of the solid salt pure *d* pipecoline could be separated by distillation with caustic soda ($\alpha_D = 31\ 9°$ for 1 dm.), the *l*-base could not be isolated. Marckwald[3] added to the sirup of the *d*-bitartrate of the racemic base crystals of *r*-pipecoline racemate ($C_6H_{13}N\ C_4H_6O_6 + H_2O$, monoclinic) by which crystallization of *d*-pipecoline-*d*-bitartrate ($C_6H_{13}N\ C_4H_6O_6 - 2H_2O$, monoclinic, hemimorphous) was induced. This phenomenon is singular as the two salts are different with respect to crystalline form and amount of water. By rubbing the crystal magma with a little water, draining with the pump, dissolving in a little hot water (about 4 cc to 10 grams of salt) and cooling the *d*-*d* salt was obtained perfectly pure. After separating a further small amount of crystallizable substance from the mother-liquor, the separated sirup was distilled with caustic soda and the collected mixture of a small amount of the *d*-base with much of the *l*-base was converted into bitartrate by the addition of *l*-tartaric acid. Crystals of *l*-pipecoline-*l*-bitartrate now separated. By again separating the bases from the mother-liquor and treating first with the *d*- and then with *l*-tartaric acid a nearly quantitative separation of the *r*-pipecoline into the active forms ($\alpha_D = \pm\ 32°$ for 1 dm.) was reached.

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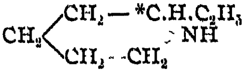
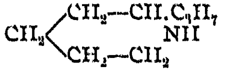
[1] Marckwald, Ber d chem Ges, **29**, 43

[2] Ladenburg Ann Chem (Liebig), **247**, 65

[3] Marckwald Ber d chem Ges., **29**, 43

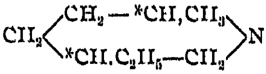
β-Pipecoline.—The solution of the bitartrate evaporated on the water-bath, yields racemic crystals, but by slow evaporation in the cold, crystals of the *l*-base are formed. The *d*-base was not secured (Ladenburg).[1]

α-Ethylpiperidine,  $CH_2\langle{CH_2—*C.H.C_2H_5 \atop CH_2—CH_2}\rangle NH$.—By the aid of *d*-tartaric acid, the *d*-base may be obtained pure (Ladenburg).[2]

α-N-Propylpiperidine,  $CH_2\langle{CH_2—CH.C_3H_7 \atop CH_2—CH_2}\rangle NH$.

Synthetic conine.—This was obtained by Ladenburg[3] from α-propylpiperidine as follows: To the concentrated, but not sirupy solution of the *d*-bitartrate, small crystals of the *d*-conine-*d*-bitartrate were added. (These, as obtained by Schorm[4] from natural conine, were rhombic crystals having the composition, $C_8H_{15}N.C_4H_6O_6 + 2H_2O$.)

A crystal magma formed from which, by pressing and recrystallizing, the *d*-base was obtained pure, and showing the same rotating power as the natural conine, $[\alpha]_D$ + 18.3°. It is also possible to evaporate the moderately dilute solution of the tartrates of the racemic base at the ordinary temperature and then purify by repeated crystallization, the crystals of *d*-conine-*d*-bitartrate which separate first.[5] The *l*-form was not obtained in pure condition.

Copellidine,  $CH_2\langle{CH_2—*CH,CH_3 \atop *CH.C_2H_5—CH_2}\rangle NH$.—By evaporating the aqueous solution of the tartrates, the salt of the *d*-base crystallizes first. The rotation of the alkaloid is $[\alpha]_D$ + 36.5° The *l*-form was not obtained pure (Levy and Wolffenstein).[6]

Isocopellidine.—From the solution of the bitartrates, the salt of the *l*-base crystallizes first, $[\alpha]_D$ — 25.9°. The *d*-base could not be obtained pure (Levy and Wolffenstein).

Propylenediamine, $CH_3—*CH.NH_2—CH_2NH_2$.—One mole cule of the base dissolved in water with two molecules of tartaric acid deposits crystals on evaporating, which contain the *l*-base, $[\alpha]_D = -20.96°$.—The *d*-base was not obtained (Baumann).[1]

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[1] Ladenburg. Ber. d. chem. Ges., **27**, 75.

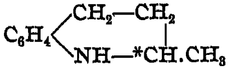
[2] Ladenburg: Ann. Chem. (Liebig), **247**, 71

[3] Ladenberg: Ber. d. chem. Ges., **19**, 2582; Ann. Chem. (Liebig), **247**, 85.

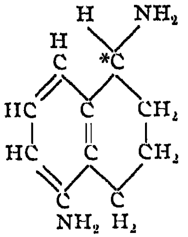
[4] Schorm: Ber. d. chem. Ges., **14**, 1768.

[5] Ladenburg: *Ibid.*, **27**, 3065.

[6] Levy and Wolffenstein: *Ibid.*, **28**, 2270.

Tetrahydroquinaldine,  $C_6H_4\langle\begin{matrix}CH_2—CH_2\\ |\\ NH—{}^*CH.CH_3\end{matrix}$ —The aqueous solution of the bitartrate yields monoclinic hemimorphous crystals of the salt containing the *d*-base. The rotation of the base is $[\alpha]_D = +56°$. The *l*-base is not known (Ladenburg).[2] [See below. Tr].

1, 5-Tetrahydronaphthylenediamine.—The aqueous solution of the *d*-bitartrate, evaporated to a sirup, and treated with a small crystal of *d*-conine-*d*-bitartrate, furnished a deposit of crystals which held the *l*-base Rotation of the salt $[\alpha]_D = -7.5°$ for $p = 3.96$ After standing several months, the separated mother-liquor furnished crystals of the bitartrate of the *d*-base Rotation of this salt $[\alpha]_D = +8.15°$ for $p = 2.44°$ (Bamberger)[3]



α-Phenylethylamine, $C_6H_5{}^*CH.CH_3.NH_2$—The separation as bitartrate was tried first by Kraft,[4] but without success, and later by Lovén[5] who succeeded The concentrated hot solution gave, on cooling, needle-shaped crystals with 1½ H_2O, from which the impure, slightly dextrorotatory base was separated; from the mother-liquor prismatic anhydrous crystals slowly separated which furnished a strongly left-rotating base

c. Resolution by Stronger Acids

Pope and Peachey[6] have recently suggested the use of strong optically active acids as agents of resolution in place of tartaric acid. *d*-*α*-chlorcamphorsulphonic acid, *d*-*α*-bromcamphorsulphonic acid and *d*-camphorsulphonic acid are compounds which suffer relatively great dissociation in aqueous solution and in their action with weak bases may be compared to the mineral acids. Among other applications the following may be quoted:

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[1] Baumann: Ber. d. chem. Ges., 28, 1179

[2] Ladenburg · *Ibid.*, 27, 76

[3] Bamberger; *Ibid.*, 23, 291

[4] Kraft; *Ibid.*, 23, 2783.

[5] Lovén: *Ibid.*, 29, 2313.

[6] Pope and Peachey: J. Chem. Soc., 73, 893 and 75, 1066.

Tetrahydropapaverine, $C_{20}H_{25}NO_4$—By combining the racemic base in aqueous solution with the calculated amount of *d*-*α*-bromcamphor sulphonic acid and warming to effect solution the combination, $C_{20}H_{25}NO_4.C_{10}H_{14}BrO.HSO_3$, is formed. On cooling long needles of the *l*-salt separate, as this is the less soluble. On concentrating and cooling again more of the salt may be secured. For the purified crystals $[\alpha]_D$ — 30° was found In the mother-liquor the *d*-salt is left but could not be obtained in pure crystalline form.

By decomposing the *l*-salt with ammonia the *l*-base is obtained $[\alpha]_D = -143.4°$. From the resinous *d*-salt the corresponding base with $[\alpha]_D = +153\ 7°$ was secured (chloroform).

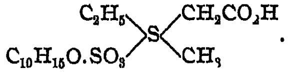
In the same resolution *d*-*α*-chlorcamphorsulphonic acid was employed also with good results.

The authors tried Reychler's camphorsulphonic acid, but the salts formed remained in a very soluble sirupy form and could not be well separated

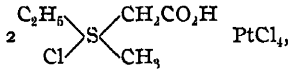
Tetrahydroquinaldine, $C_{10}H_{13}N$.—This was resolved by the aid of *d*-*α*-bromcamphorsulphonic acid as described above. An alcoholic solution of the *l*-salt gave $[\alpha]_D$ - $+41\ 5°$ For the base, separated by distillation in a current of steam with a slight excess of soda, $[\alpha]_D = -58.12$ was found.

Camphoroxime, $C_{10}H_{16}.NOH$.—The racemic oxime was resolved by action of *d*-camphorsulphonic acid. Sixty grams of the oxime and 90 grams of the sulphonic acid were mixed in boiling acetone. On cooling a crystalline precipitate forms and more may be obtained from the mother-liquor. On recrystallizing the whole of the fractions from boiling ether two products are finally obtained, the less soluble being *d*-camphoroxime *d*-camphorsulphonate, and the more soluble the *l*-camphoroxime *d*-camphorsulphonate. For the first $[\alpha]_D = +4.3°$ was found ($c = 1.7508$ in absolute alcohol) and for the oxime from it $[\alpha]_D = -41.3°$. The oxime from the *l*-camphor oxime *d*-camphor sulphonate gave $[\alpha]_D = +41.7°$.

The resolution of α-benzylphenylallylmethyl ammonium iodide was likewise accomplished by aid of *d*-camphor sulphonic acid[1] (see § 14) and very recently the same authors have described the resolution of an asymmetric sulphur compound by use of this optically active sulphonic acid.[2] This compound is methylethylthetine and from the bromide by addition of the silver salt of *d*-camphorsulphonic acid the corresponding *d*-methylethylthetine *d*-camphorsulphonate was obtained. This has the composition:



By decomposing the alcoholic solution of this salt by addition of hydrochloric acid and platinum chloride, the platinum compound,



is obtained, for which $[\alpha]_D = +4.6°$ was found ($c = 1.34$, water)

Resolution by Esterification or Saponification.

The processes first described are properly physical, as no real chemical alteration follows in the combinations to produce new crystalline structures Essentially different in principle is a method recently worked out by Marckwald and McKenzie.[3]

Two optically active antipodes must, in general, exhibit the same behavior in all chemical reactions But this no longer holds if the reaction takes place between them and another asymmetric compound If the change in question is one which, like the formation of a salt, depends simply on the affinity of acid and base, no difference may be observed, but on the other hand, a difference may be expected in proportion as the progress or direction of the reaction is dependent on the space relations of the atoms in the molecules of the combining substances In particularly marked degree, the formation of esters is a reaction of this nature. The rapidity of esterification depends to a remarkable degree on the structure of the carbon chain of the acid. The velocity of esterification for the acids of the type, $R.CH_2CO_2H$, is about twice as great as for the acids of the type, $R'R''.CH.CO_2H$, and much greater than for the acids, $R'R''R'''C.CO_2H$.

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[1] J Chem Soc, 75, 1127.

[2] Pope and Peachey: *Ibid*, 77, 1072.

[3] Marckwald and McKenzie; Ber d chem Ges, 32, 2130 (1899)

These relations while pronounced in the aliphatic acids are more clearly marked among some of the aromatic acids, a fact which was pointed out by v. Meyer.[1] It would appear probable, therefore, that the velocity of esterification of two oppositely active acids with the same optically active alcohol might not be the same. This question, Marckwald and McKenzie tested by a simple experiment. Equivalent molecular amounts of racemic mandelic acid and menthol were heated for an hour to 155°, and at the end of the time, the uncombined acid was separated from the reaction product. It was found to be left-rotating, from which it follows that *l*-mandelic acid forms an ester with *l* menthol more slowly than *d*-mandelic acid.

In a practical experiment 50 grams of *r* mandelic acid and 50 grams of menthol were heated to 155° through one hour. In the reaction mass the unchanged acid was separated by dilute ammonia, and finally, after separating traces of the esters and menthol with it, the mandelic acid was precipitated by sulphuric acid. The recovered acid was taken up completely by ether and after evaporation of the ether was found to weigh 33.8 grams. The specific rotation was found to be $[\alpha]_D = -3.3^\circ$, showing that it now contained 0.72 gram of *l*-mandelic acid. In the paper quoted, the authors describe the separation and identification of this acid in pure form.

Experiments were then made with the mixture of esters and unchanged menthol left in ether solution after separation of the uncombined mandelic acid. The ether was evaporated, the residue mixed with 3.5 grams of potassium hydroxide in solution and boiled some hours. This liquid was evaporated and treated with water to dissolve the potassium salt. The solution obtained was heated to drive out traces of menthol, treated with sulphuric acid and extracted with ether. In this way a mandelic acid was obtained as a saponification product, and amounted to 8.7 grams. Its specific rotation was $[\alpha]_D =$

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[1] v. Meyer: Ber. d. chem. Ges., **27**, 1580; **28**, 1254.

+ 3.1°, indicating the presence 0.164 gram of the *d*-acid. The remaining menthyl ester was treated with alcoholic potash now to complete saponification and the mandelic acid separated as before. 2.7 grams were obtained and this had a specific rotation of $[\alpha]_D = -10.4°$, corresponding to 0 188 gram of *l*-mandelic acid.

The authors have therefore demonstrated the possibility of resolution by their general processes They point out further that their application may be expected in the resolution of racemic alcohols rather than of acids, for which the other methods are more convenient.

3. Resolution by Aid of Fungi

34. As already mentioned in § 19 this separation depends on the phenomenon that when in solutions of racemic bodies spores of certain fungi are sowed and allowed to grow, one of the antipodes disappears while the other remains untouched. Only one of the two active forms is thus secured

A number of general observations on the mode of action of the fungi have already been made. In this place we are concerned with certain matters, which, inasmuch as they have received but little consideration in the chemical literature, call for a detailed discussion.

Data on the Fungi Suitable for Resolution Pure Cultures and Methods of Experimentation

BY DR P LINDNER

Since, by aid of pure culture methods, proof has been given by the biological work of the last decade, that the mode of development of most of the lower fungi presents a certain constancy and is by no means as complex as was formerly supposed, the question of species has again assumed greater importance and interest The mycologist of to-day will no longer risk designating the green growth on a piece of bread or orange peel as *Penicillium glaucum*, without previously informing himself by microscopic examination or by cultures. It has been found possible to establish a large number of species which have the green color of the spore masses in common, but which in spite of apparent macroscopic similarity in form show distinct differences from a morphological and biological standpoint.

When one has to refer to data in the older literature on *Penicillium glaucum* he must always feel uncertain as to whether the author consulted had in hand the organism now so designated or something else.

Also the statements concerning yeasts in the older literature must to-day be received with caution. Wine yeast, for example, has been often used for splitting racemic bodies. But we know now that common wine yeast may be a mixture of many different varieties. If some one of these should be furnished us in the form of a pure culture it could happen that a very different result would follow from a splitting experiment from one previously recorded.

In view then of our advanced knowledge in the consideration of the fungi the task of studying each one in isolated pure form and determining its action on nutritive media becomes of the first importance.

Scientific aspirations in this direction are greatly advanced by the fortunate circumstance that there are mycologic institutes like that of Kral (Prague, Kleiner Ring) which collect the various species discovered and described by different authors, make pure cultures of them and preserve them there for sale

It remains then for the experimenting chemist to protect the pure culture, as received, from infection, and to increase it in such a manner, that the substance to be investigated may be brought completely under its action. It will be explained below how all this may be most conveniently done.

As, however, there is no difficulty in securing spores of fungi from the air or water, and bringing them into the condition of pure cultures, one may often proceed to a certain degree independently. Care should be taken to submit finally a portion of the pure culture to a mycologist for exact determination of species before publishing the results of investigations.

How may the spores contained in the air, or water, or other liquid be recognized and obtained pure? Suppose we wish to examine the air of the laboratory for fungi. We can employ crystallization dishes or glass cylinders. Two dishes, one fitting over the other, or a glass cylinder closed with a plug of cotton, are placed in the oven and heated two hours to a temperature of about 150° C , the flame under the oven is extinguished, and the glasses are allowed to cool in it. When this is accomplished, we allow the lower dish or glass cylinder (such a cylinder as is used with a specific gravity spindle) to stand open one to two hours In this time a number of fungus spores settle from the air onto the inner glass surfaces. On account of their minuteness, these are not visible to the eye, and because of their relatively small number, they can not be found by a strong magnifying glass or with the microscope But they become distinctly visible when a proper food is offered them, best a nutritive gelatine. Most conveniently beer-wort gelatine or plum-decoction gelatine may be prepared To 1 liter of beer-wort or plum-decoction (each with about 10 to 15 per cent. of extract) about 100 grams of fine white gelatine may be taken The gelatine mixture, prepared by dissolving at water-bath heat and filtering, is filled into test-tubes which are plugged with cotton, and then exposed to steam heat one-half hour(in a Koch's sterilizer)

The contents of a test-tube is poured at a temperature of 20° to 30° C., into the exposed glass dish or cylinder The first, with its cover in position, after the hardening of the gelatine, is placed in a moist chamber, that is, under a bell-jar, the air in which is kept moist by wet filter-paper or by equivalent means The gelatine poured into the glass cylinder is allowed to harden around the sides, which may be accomplished by holding the vessel in a nearly horizontal position and allowing cold hydrant water to flow over it, it being meanwhile slowly rotated to effect an even distribution After two or three days a growth begins to appear everywhere in the gelatine where the spores lie embedded, and this later develops to a branching mycelium. In the majority of cases, these mycelia are pure, that is, other organisms have not grown in with them. Sufficient indication of this is usually given by ocular examination alone. The term '*mycelium*' is applied to the sum of the threads or hyphae growing out of the fungus spore. While some of these play the part of rootlets, others grow in the air (so-called air hyphae) and develop to fructification (Fig. 6). The following illustration

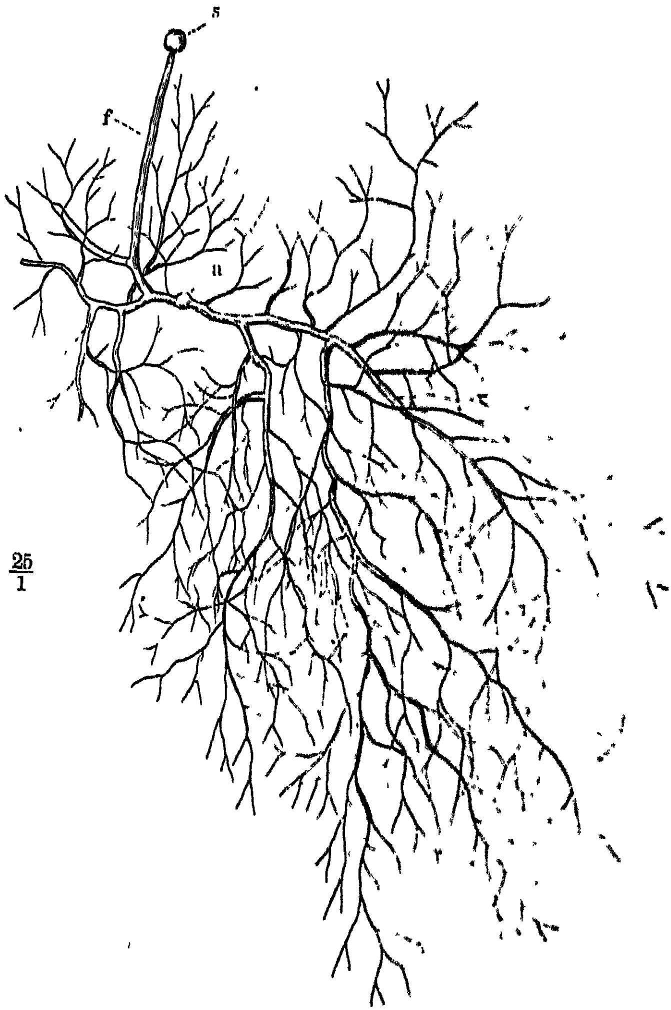

Fig. 6. *Mucor Mucedo*.—Form and ramifications of a full grown *Mycelium*, developed from the spore, *a*. *f* is the fruit stem and *s* the sporangium. After Brefeld.

gives a clear representation of these relations. This shows a kind of mucor (*Mucor Mucedo*), which may be easily obtained from bread, malt, horse-dung and decaying fruits kept in moist places. At *a* is shown the developed spore; *f* is an air-hypha which at its end is in the act of forming a spore-case or so-called sporangium With darkening in this spherical organ maturity is reached. If we touch it with a previously sterilized needle, the sporangium skin breaks and a large number of spores cling to the needle. If this is now dipped into sterile nutritive solution, a new development of spores begins similar to that just described. In a few days the whole liquid is permeated by the fungus filaments, and on the surface, new air-hyphæ appear and grow toward fructification. Figure 7 shows the structure of the sporangium The external wall or skin is covered with numerous small crystalline needles of calcium oxalate The club-like bunch shown in the center is the so-called columella (little column), it is shown free in Fig 8 after the sporangium has been broken and emptied. The columella is originally a simple transverse wall which separates the sporangium from the sporangium stem

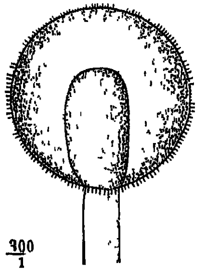

Fig 7 *Mucor Mucedo* Young fruit stem

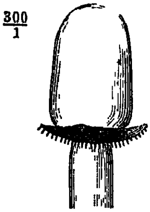

Fig 8 Old fruit stem Brefeld

If in the study of the air a spore of *Penicillium glaucum* had become imbedded we would not observe as fine a development of air-hyphæ Fructification begins early and a very low turf only is formed which becomes covered with masses of white spores turning later to bluish green. Under the microscope we can see on the ends of the air-hyphæ the growth of lateral bunches or branches with finger-like spore-supporting organs, so-called sterigmata. When a spore is fully developed a new one is immediately formed, which remains loosely united to the first. This process repeats itself and by undisturbed growth gives rise to beautiful spore chains resembling strings of pearls and containing fifty or more members. See Figs. 9

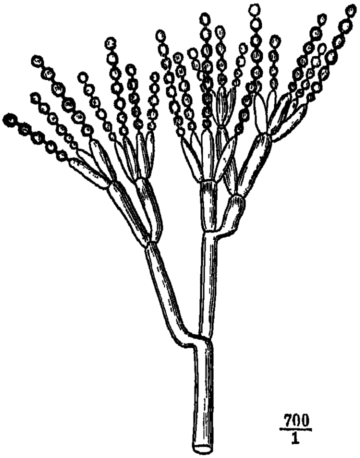

Fig 9 *Penicillium glaucum* Hyphæ. (From Brefeld, Bot Unters über Schimmelpilze, 1 Heft, 1872)

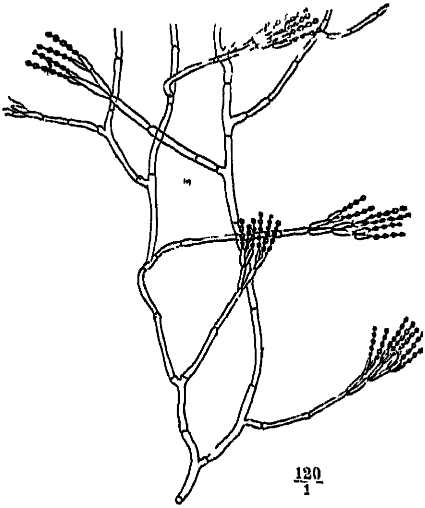

Fig 10 Piece of asexually fructifying *Penicillium* Mycelia From Brefeld

and 10. Fig. 10 further shows that this mold, as distinguished from *Mucor Mucedo*, contains transverse walls in the stem in large numbers; in other words the stems are divided

In order to take these spores from the spore case by the aid of a needle this is best dipped first in the nutrient medium or in sterile water.[1] The spores are dry and would not cling to a dry needle very well; but, as distinguished from *Mucor* spores, they are not moistened immediately as the contents, and apparently the membrane also contains fat. They distribute themselves uniformly over the droplet on the needle-point in the form of a thin dry layer. In consequence of these peculiarities this mold is spread very rapidly through the air ; the physiologist attempting to produce pure cultures has much to fear from its ubiquity.

In appearance and behavior *Aspergillus glaucus*, Fig. 11, stands close to *Penicillium glaucum*. Here, also, long spore chains grow on sterigmata, but the latter are all situated on club-like expansions of the undivided fruit stalk. Several varieties have also branched sterigmata,—the *Sterigmatocysti.*

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[1] The distilled water of the laboratory is not sterile; it often contains 100,000 or more germs to the cubic centimeter.

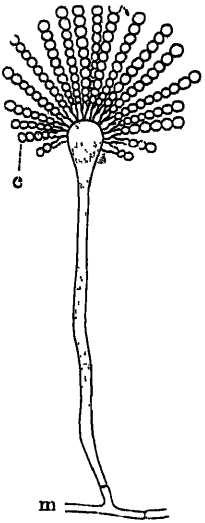

Fig 11
Aspergillus glaucus
(Eurotium herbariorum)
c Spore-chain, *m* Mycel
After Kny, wall charts

Frequently mycelia develop on the gelatine unaccompanied by fructification, even with *Penicillium* and *Aspergillus* varieties. As broken-off pieces of the filaments are capable of growth, it is sufficient to pick up a little of the mycelium with a needle and deposit it in a nutrient medium

While the common molds as *Penicillium glaucum*, *Aspergillus glaucus*, and others, may nearly always be obtained from the air, *yeasts* are found less often. As these find the most favorable conditions of growth in nature on sweet fruits, it follows that they are most commonly met with in the autumn. As compared with the mold mycelia, they grow almost invisibly in the nutrient gelatine, and especially in the form of small, white pinhead-like colonies It is only occasionally that one finds colonies that are spread out superficially; these consist then generally of aerobiotic mold yeasts It is very difficult, even by the aid of the microscope, to determine directly what form of yeast one has found In order to reach a certain comparison with forms already known, there is required usually a long series of culture experiments which may consume weeks or months If one desires to further cultivate one of the colonies found in the gelatine in a new nutrient solution, the inoculation must take place with a sterilized needle. It is sufficient if only a part of a colony remains clinging to the needle, as this much will contain thousands of cells capable of development.

That which appears to us very strange in the behavior of the yeasts is the fact that physiologically very differently acting forms exhibit almost no differences in the appearance of their cells. After having mixed four or five different varieties in a little drop, we are often no longer able from the microscopic image to pick out the separate cells The cell forms, Figs. 12 to 14, which represent *S. ellipsoideus*, may be found in a large number of beer and wine yeasts. Simple pictures or drawings of the cells are therefore quite insufficient as a means of characterizing a definite yeast variety

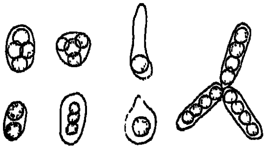

Fig 12 *Sacchar. ellips* Conidia in which internal formation of spores has begun

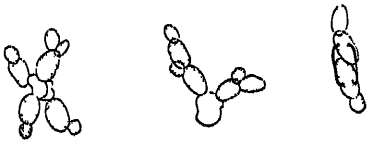

Fig 13 *Sacchar ellips* Developed spores. After Brefeld from F v. Tavel · "Morphologie der Pilze." Jena 1892

The distinction between yeast cells in budding condition offers the same difficulties as the distinction between mold mycelia in which no special seed forms have been developed

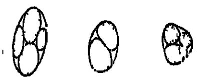

Fig 14 *Sacchar ellips* Sporangia the spores in which are swollen for germination After Brefeld

With the yeasts, besides by budding, there is a second method of fructification, *viz.*, through the formation of endogenous spores. This form of seed which is shown in the two illustrations never comes to development in fermenting liquids, and then also on account of its morphological simplicity it affords few characteristic points of differentiation to settle the question of species. In germination the spore passes immediately to the budding condition again

In making use of the yeast colonies obtained in air investigations it is necessary to recognize that while in all probability we have secured pure material, a certain guarantee for it is lacking. This can be secured only by the method introduced by Hansen of cultivation from a cell. With yeasts this method of cultivation may be applied without difficulty. But with the bacteria it often fails because of their extreme minuteness. However, the colonies grown in gelatine, as distinguished from the yeasts, present often characteristic color differences, so that by the eye alone a conclusion may be reached as to different forms present by the simple variations in their gross appearance. A greater variety in general is observed also with respect to shape and size of the single cells. By aid of the methods of pure culture it has been found, as with the yeasts and molds, that what were formerly regarded as simple forms may be resolved into several species. So, for example, the *Bacterium termo* of the older authors is no longer regarded as a single species, but the name is used as a collective description. The different varieties of *Proteus*, as *P. vulgaris*, *Zenkeri*, *hominis*, exhibit about the same behavior that was formerly given as characteristic of *B. termo*. For bacteria also the rule is true that it is easier to obtain a pure culture than to determine its species

From the remarks just made, it appears clear that the investigations of the older authors on the action of organisms on racemic bodies must be repeated under such conditions that only pure cultures and germ-free solutions may be employed, and further that care must be taken to prevent the ingress of any infection during the progress of the experiment.

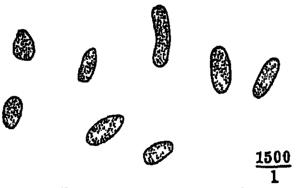

Fig 15 *Bacterium termo* (Bacterium pseudotermo) After A Fischer, Pringsh Jahrb 27, 1 (1895)

To make a nutrient solution germ-free is not difficult ; it is simply necessary to boil it a long time or frequently for short intervals, the neck of the flask being closed by a wad of cotton. This last may be dispensed with in the so-called Pasteur flask, the neck of which is continued by a long bent tube

Formerly, experiments on resolution or splitting were usually carried out by mixing the racemic body, 3 to 5 grams to the liter, with nutrient salts , *e g* , with one gram of potassium phosphate and 0.2 gram of magnesium phosphate In working with molds, a little phosphoric or sulphuric acid was added to prevent the rapid growth of bacteria A small amount of the special organism used was sowed in This must then grow gradually and develop its splitting power. It appears to me to be better to add no nutrient salts to the solution of the racemic body, but to seed the organism employed in larger amount. This should be previously grown in a specially good nutrient solution In the case of yeasts, for example, the cells could be cultivated in sterilized wort or wine-must, the fermented liquid poured off, and the residue washed with sterilized and cooled distilled water. To the vessel containing the racemic body, the so-purified yeast material is then added. The action is much more rapid, and the development of accidentally admitted germs avoided. Molds may be similarly separated from the nutrient solution. But the preparation of an active bacterial sediment offers greater difficulties. I employ for this purpose long glass tubes, 5 or 6 centimeters wide, narrowed at each end, which are completely filled with the turbid nutrient solution and placed in a horizontal position The sediment finds now a large surface for settling and collects here as a relatively firm layer which almost wholly remains when the liquid is poured away. The sterilization of the tube is effected by steaming and subsequent addition of a sterilized cotton plug The nutrient solution poured off from the sediment (accomplished by forcing air in through the cotton filter), may be replaced directly by the solution of the racemic body After sufficiently long action the liquid may be drawn off and fresh added This arrangement of the experiment which would be suitabl also for yeasts and molds, as the air necessary for the growt of the organisms may easily be forced in through the cotto filter, permits continuous operation to a certain degree Wit the molds, the tube should not be quite filled with liquid, bu an air space should be left in which an active mold surfac may be formed With these conditions it is likely that th solution under experiment could be allowed to flow throug slowly and continuously The action here should be, for th reason, a very rapid and complete one, as organism and liqui offer a large contact surface.

Information concerning the preparation of nutrient solu-tions and nutrient gelatine, the sterilization of vessels an liquids, the production of pure cultures and the further cult vation of the same in larger apparatus on the technical scale ma be found in the work of Lindner: "Mikroskopische Betriebscontrole in den Gährungsgewerben mit einer Einführung i die Hefereincultur, Infectionslehre, und Hefenkunde. M vier Lichtdrucktafeln und 105 Textabbildungen. Verla Paul Parey, Berlin." On molds and their cultivation muc information will be found in the work of Wehmer: "Beiträg zur Kenntniss einheimischer Pilze." In Part I, the citric aci producing molds are discussed and the green molds thus far described of the genera *Aspergillus* (*Eurotium*) *Sterigmatocystis*, *Penicillium* and *Citromyces* are compared in tabular form. Part II treats specially of the rotting of fruit and the varieties of fungi which grow preferably on or in solutions of organic acids. Part III (which has not yet appeared, 1898) will contain a monograph of the genus *Aspergillus* Part I was published in 1893 by Hahn, Hannover and Leipzig, the following parts by Gustav Fischer, Jena Finally, attention must be called to the book by Zopf, "Die Pilze," Breslau, 1890, published by Edward Trewendt, as the chapter on physiology has been well worked out

To chemists who wish to concern themselves with the study of racemic bodies it may be recommended to visit fermentation laboratories such as are found in Berlin, Munich, Vienna, Copenhagen, New York, Chicago, and elsewhere It may be possible to obtain from these even large quantities of pure cultures of yeasts or fungi materials

According to a compilation by Winther[1] the following active forms have been obtained by the aid of fungi

l-Tartaric acid by Pasteur[2] from ammonium racemate by addition of a spontaneously fermented ammonium tartrate solution, and then by aid of *Penicillium glaucum* [3]

d-Tartaric acid was obtained by Lewkowitsch[4] by the action of an unidentified schizomycete (*vibrio*), occurring in impure *Penicillium* cultures, on ammonium racemate

l-Glyceric acid from the racemic ammonium salt by aid of *Penicillium glaucum* (Lewkowitsch) [5]

d-Glyceric acid was obtained by Frankland and Frew[6] from *r*-calcium glycerate, to whose solution peptone, salts and calcium carbonate were added, by the action of *Bacillus ethaceticus*. Left-rotating calcium glycerate is produced which yields right-rotating free glyceric acid by treatment with oxalic acid. After long heating on the water-bath, solutions

[1] Winther Ber d chem Ges , **28**, 3022.

[2] Pasteur: Compt rend , **46**, 615 (1858).

[3] Pasteur *Ibid* , **51**, 298 (1860)

[4] Lewkowitsch: Ber d chem Ges., **16**, 1572.

[5] Lewkowitsch: *Ibid* , **16**, 2720.

[6] Frankland and Frew: J. Chem Soc , **59**, 96

of the acid yield a slightly soluble left-rotating anhydride.

d-Lactic acid was obtained by Lewkowitsch,[1] also by Linossier[2] from fermentation ammonium lactate by the action of *Penicillium glaucum* P. Frankland and MacGregor[3] observed the formation of left-rotating calcium lactate, which furnished the right-rotating free acid, in the spontaneous fermentation of solutions of the racemic calcium salt to which calcium carbonate, peptone, and nutritive salts had been added Sarcolactic acid rotates to the left.

d-Ethoxysuccinic acid was obtained by Purdie and Walker[4] from the *r*-ammonium salt by *Penicillium glaucum*. The salts also are right-rotating.

l-Aspartic acid.—A moldy solution of the *r*-acid in the air becomes left-rotating (Engel).[5]

l-Glutaminic acid split off by *Penicillium glaucum* (Schulze and Bosshard,[6] Menozzi and Appiani).[7]

Active leucine, rotating to the right in water, and to the left in hydrochloric acid solution, was obtained from the racemic product by Schulze and Likiernik[8] by the aid of *Penicillium glaucum*, the racemic compound having been formed by the action of hydrocyanic acid on isovaleraldehyde ammonia It was obtained also from the *r*-compound produced from fermentation of caproic acid (Schulze) [9]

By the use of beer yeast the following have been obtained from racemic sugars.

l-Glucose (E. Fischer),[10]
l-Mannose (E. Fischer),[11]
l-Galactose (E. Fischer and Hertz),[12]
l-Fructose (E. Fischer).[13]

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[1] Lewkowitsch Ber. d. chem. Ges., **16**, 2720.
[2] Linossier Bull. Soc Chim, [3], **6**, 10
[3] Frankland and MacGregor: J. Chem. Soc, **63**, 1028.
[4] Purdie and Walker · *Ibid*, **63**, 229.
[5] Engel · Compt. rend., **106**, 1734.
[6] Schulze and Bosshard · Ztschr physiol Chem, **10**, 143.
[7] Menozzi and Appiani · Chem. Centrbl., 1894, **1**, 674.
[8] Schulze and Likiernik: Ber. d. chem. Ges., **24**, 671.
[9] Schulze · *Ibid*, **26**, 56; Ztschr. physiol. Chem., **10**, 138.
[10] Fischer: Ber. d. chem Ges., **23**, 2620
[11] Fischer: *Ibid*, **23**, 382.
[12] Fischer and Hertz: *Ibid.*, **25**, 1259.
[13] Fischer: *Ibid.*, **23**, 389; **27**, 2031.

l-α-Propyleneglycol was formed in a 3 per cent. aqueous solution of the racemic compound made from glyceric acid after sowing an impure fungus culture from cheese, in which *Bacterium termo* was abundantly present. The preparation must be perfectly freed from empyreumatic matters Propionic and lactic acids were found as products of the fermented part (LeBel).[1]

The following active alcohols have been made from dilute aqueous solutions of the synthetic preparations and all by aid of *Penicillium glaucum*

l-Methylethyl carbinol (Combes and Le Bel),[2,3]
l-Methyl-N-propyl carbinol (Le Bel),[3]
l-Methylbutyl carbinol (Combes and Le Bel),[2]
d-Ethylpropyl carbinol (Combes and Le Bel),[2,3]
d-Methyl-N-amyl carbinol (Le Bel) [3]

d-Methylethyl carbincarbinol was obtained through fungi from a mixture of *r*- and *l*-amyl alcohol with destruction of the latter (Le Bel) [4]

d-Mandelic acid was obtained by Lewkowitsch[5] by addition of a few spores of a pure *Penicillium* culture to a solution of 3 grams of the *r*-ammonium salt in a liter of water containing 1 25 grams of nutrient salts with a little sulphuric or phosphoric acid and carefully sterilized

l-Mandelic acid was formed in nine out of twelve experiments by application of an impure *Penicillium* culture, in which *S ellipsoideus* and an undetermined fungus (vibrio?) were finally recognized in the liquid (Lewkowitsch).[6] The acid from amygdalin is left-rotating.

d-Cinnamic acid dichloride has been separated by aid of *Aspergillus fumigatus* and also by yeast (Stavenhagen and Finkenbeiner).[7]

l-Isobutylpropylethylmethyl ammonium chloride was obtained by Le Bel[8] from the synthetic compound by use of a *Penicillium* culture which was not quite pure.

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[1] Le Bell: Bull. Soc Chim., [3], 9, 678, Compt. rend., 92, 532

[2] Combes and Le Bel. Bull Soc Chim, [3], 7, 551

[3] Le Bel: *Ibid.*, [3], 9, 676.

[4] LeBel · Compt. rend, 87, 213

[5] Lewkowitsch. Ber d. chem. Ges, 15, 1505; 16, 1569

[6] Lewkowitsch; Ber d. chem Ges, 16, 1571.

[7] Stavenhagen and Finkenbeiner Ber. d. chem Ges, 27, 456

[8] Le Bel: Compt. rend., 112, 725.

E. Formation of Active Isomers

35. **1. From Inactive Materials. Artificial Preparation of Active Compounds.**—The phenomenon, that active bodies as occurring in nature were always found to be inactive when prepared synthetically, led formerly to the opinion that substances endowed with the power of optical rotation could be produced only within the animal or vegetable cell. This view which was maintained particularly by Pasteur[1] had to be abandoned when in 1873 Jungfleisch[2] succeeded in producing tartaric acid completely by synthesis, starting with ethylene which was converted into the dibromide, ethylene cyanide, succinic acid, dibromsuccinic acid and finally racemic acid, which was split up into active components. Since it has been recognized that the inactivity of asymmetric synthetic compounds depends on their racemic structure, many of them have been produced in active forms. Among such which are found in nature, conine may be especially referred to, the complete synthesis of which was accomplished by Ladenburg in the following manner[3] Starting with acetic acid this is converted into acetone, isopropyl alcohol, glycerol, allyl bromide, trimethylene bromide, trimethylene cyanide, pentamethylene diamine, piperidine, pyridine, *α*-picoline, *α*-allyl pyridine and finally into *α*-propyl piperidine = *r* conine, from which by splitting with tartaric acid the *d*-form, identical with the natural conine, is secured

A special method for the synthesis of active compounds, has recently been tried by Boyd[4] as he attempted to determine whether, when asymmetric bodies were formed in a magnetic field, one of the antipodes would not be predominant, leaving the product endowed with rotating power and not racemic. Benzoyl formic acid was converted into mandelic acid by treatment with sodium amalgam in vessels kept in a magnetic field of 7,000 to 8,000 C. G. S. units, but it was found that the product was quite inactive, and also when the reaction was carried out in presence of active substances, such as *d*-tartaric acid or *l*-mandelic acid. Likewise, in the bromination of stilbene, racemic stilbene bromide was formed. The magnetic rotation to which the molecules are subjected during formation, leaves no permanent result.

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[1] Pasteur: Compt. rend , 81, 128.

[2] Jungfleisch: Bull. Soc. Chim. [2], 19, 194; Compt. rend., 76, 286.

[3] Ladenburg: Ber. d. chem. Ges., 22, 1403; Ann. Chem. (Liebig), 247, 80.

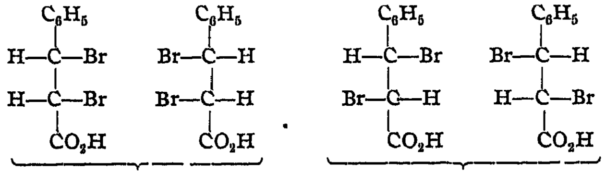
[4] Boyd: Inaug. Dissertation, Heidelberg, 1896.

Relative to the synthesis of active substances, these conditions follow from the doctrine of asymmetric carbon atoms as first pointed out by van 't Hoff (Chimie dans l'espace, 1875, p. 20–28) :

a. If a compound formed from a symmetric substance has but one asymmetric carbon atom, then a single racemic body always results. The same is true when the molecule of a resulting active compound contains two asymmetric carbon atoms, but consists of two similar halves. For example, from succinic acid only one racemic dibromsuccinic acid may be made.

b. If a molecule containing two asymmetric carbon atoms, but not consisting of two similar halves, is derived from an inactive substance, the production of two racemic pairs is possible, the splitting of which must lead to four active isomers It is not necessary that the two racemic bodies should be formed in equal amounts, but, because of different degrees of stability, the formation of one may be favored, and that of the other entirely suppressed.

For example, cinnamic acid, $C_6H_5CH=CH.CO_2H$, may yield the following cinnamic acid dibromides.



$$\underbrace{\begin{array}{cc} C_6H_5 & C_6H_5 \\ | & | \\ H-C-Br & Br-C-H \\ | & | \\ H-C-Br & Br-C-H \\ | & | \\ CO_2H & CO_2H \end{array}} \quad . \quad \underbrace{\begin{array}{cc} C_6H_5 & C_6H_5 \\ | & | \\ H-C-Br & Br-C-H \\ | & | \\ Br-C-H & H-C-Br \\ | & | \\ CO_2H & CO_2H \end{array}}$$

First racemic body. Second racemic body

According to Liebermann and Hartmann,[1] the inactive bromination product of cinnamic acid does not probably contain the two racemic pairs, but only one, the splitting of which up to the present time has led to antipodes with rotations, $[\alpha]_D = +55°$ and $-41°$. The other racemic compound has been obtained by Liebermann[2] by bromination of the labile allocinnamic acid, and decomposed approximately into components with $[\alpha] = +64°$ and $-71°$.

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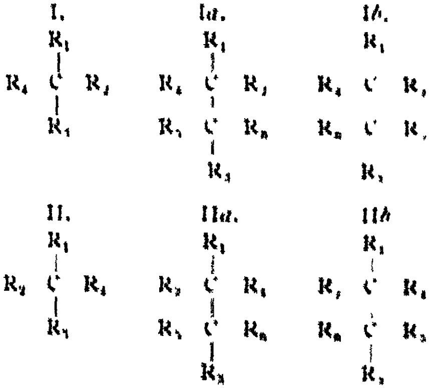
[1] Liebermann and Hartmann: Ber d chem Ges., **26**, 1664

[2] Liebermann. *Ibid.*, **27**, 2037.

36.—2. From Active Materials.—The following cases may appear:

a. A body with one asymmetric carbon atom may be converted into a compound with two such atoms. According to the van 't Hoff-Le Bel theory, an active molecule, $CR_1R_2R_3R_4$, whose right-rotating configuration is shown by I below, must furnish two isomeric products, I*a* and I*b*, which are not corresponding antipodes, by the introduction of the group, $R_5\;\overset{|}{\underset{|}{C}}-R_6$.

They possess, therefore, different properties, and may be produced in unequal amounts. Likewise from the left rotating configuration, II, the not-antipode isomers, II*a* and II*b* are formed:



$$\begin{array}{ccc}
\text{I.} & \text{Ia.} & \text{Ib.} \\
\begin{array}{ccc} & R_1 & \\ & | & \\ R_4 & C & R_2 \\ & | & \\ & R_3 & \end{array} &
\begin{array}{ccc} & R_1 & \\ & | & \\ R_4 & C & R_2 \\ & | & \\ R_5 & C & R_6 \\ & | & \\ & R_3 & \end{array} &
\begin{array}{ccc} & R_1 & \\ & & \\ R_4 & C & R_2 \\ & & \\ R_6 & C & R_5 \\ & & \\ & R_3 & \end{array} \\
\text{II.} & \text{IIa.} & \text{IIb} \\
\begin{array}{ccc} & R_1 & \\ & | & \\ R_2 & C & R_4 \\ & | & \\ & R_3 & \end{array} &
\begin{array}{ccc} & R_1 & \\ & | & \\ R_2 & C & R_4 \\ & | & \\ R_5 & C & R_6 \\ & | & \\ & R_3 & \end{array} &
\begin{array}{ccc} & R_1 & \\ & | & \\ R_2 & C & R_4 \\ & | & \\ R_6 & C & R_5 \\ & | & \\ & R_3 & \end{array}
\end{array}$$

In this case the original right- or left rotating substance does not yield a racemic body by the chemical change, but a mixture of two active isomers which must possess unequal rotating powers. The relations are therefore different from what they are in the syntheses from inactive bodies.

Among the above four isomers, each two form true antipodes; *viz.*, I*a* with II*b*, and I*b* with II*a*, which may be combined to form two racemic compounds. A mixture of these two last must result when the racemic form, I + II, of the original substance is subjected to the chemical reaction, the final product being then inactive.

As a matter of course, the case remains the same if the new asymmetric carbon atom is produced, not through addition, but from one of the symmetric carbon atoms already present in the molecule.

The above relations pointed out by van 't Hoff, may be expressed in the following manner if the two asymmetric groups in the four isomers be represented by ± A and ± B:

The original + compound furnishes the bodies: $\begin{cases} +A+B \\ +A-B \end{cases}$

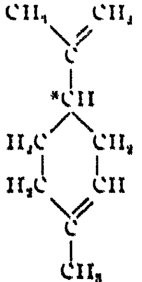
" " − compound " " " $\begin{cases} -A+B \\ -A-B \end{cases}$

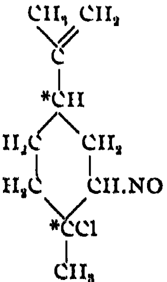
and the two pairs of antipodes are:

$$\left.\begin{matrix} +A+B \\ -A-B \end{matrix}\right\} \text{ and } \left.\begin{matrix} +A-B \\ -A+B \end{matrix}\right\}.$$

If the specific rotations of the four isomers are known, the rotating powers of the groups A and B may be calculated.

These theoretical predictions have been frequently confirmed by experiment. If, for example, limonene be converted into the nitrosochloride compound, $C_{10}H_{16}.NOCl$, by treatment with amyl nitrite and hydrochloric acid with addition of acetic acid, which, with great probability, gives,


Limonene.


Limonenenitrosochloride.

there are always formed from the latter substance, according to Wallach,[1] two isomers (α and β) which may be easily separated by their different solubilities in ether. There results from

+ Limonene $\begin{cases} \alpha\text{-nitrosochloride } [\alpha]_D = +313.4^\circ \\ \beta\text{- " " } = +240.3 \end{cases}$

− Limonene $\begin{cases} \alpha\text{- " " } = -314.8 \\ \beta\text{- " " } = -242.2 \end{cases}$

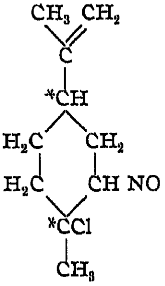
The two α-compounds on the one hand, and the two β-compounds on the other, represent optical antipodes.

[1] Wallach: Ann. Chem. (Liebig), 252, 108; 270, 171.

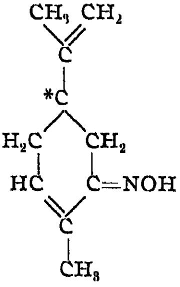
In the reaction the α-nitrosochlorides are formed in larger amounts than the β-products, the first crystallize in well-formed monosymmetric prisms which dissolve easily in ether, but decompose quickly on keeping; the latter are finely crystalline, difficultly soluble in ether, and much more stable. Chemically the α- and β-isomers behave in a similar manner; the latter, however, in benzene solution show a double molecular weight (Wallach).[1]

Dipentene (*d*-*l*-limonene) is an inactive product which is a mixture of two racemic bodies (Wallach).[2]

Of the two asymmetric carbon atoms in the limonene nitrosochlorides, one may be easily destroyed. This happens when each compound is treated with alcoholic potash solution by which, with loss of H + Cl, they become transformed into carvoximes, $C_{10}H_{14}$ NOH :



Limonenenitrosochloride.



Carvoxime

The carvoxime appears only in two forms (*d* and *l*), and therefore, from the α- and β-nitrosochloride of the same kind, the same product must result. This was found by Wallach[3] to be the case, a change in the direction of rotation following:

$$\begin{array}{llll}\text{From} + \left\{\begin{array}{l}\alpha\text{-nitrosochloride}\\ \beta\text{-} \qquad ``\end{array}\right\} & \text{results} & -\text{ carvoxime} & [\alpha]_D = -39.3,\\ \quad `` \quad - \left\{\begin{array}{l}\alpha\text{-} \qquad ``\\ \beta\text{-} \qquad ``\end{array}\right\} & \quad `` & +\text{ carvoxime} & \quad `` \; = +39.7.\end{array}$$

b. If in a body which contains several asymmetric carbon atoms, the number of the latter be increased by one, the same conditions which have just been discussed must obtain,—the new substance must exist in two isomeric forms. E. Fischer[1] has furnished the experimental proof of this as he found that from α-glucoheptose, $C_7H_{14}O_7$, ($[\alpha]_D = -19.7°$, $c = 10$, water) two different glucooctonic acids, $C_8H_{16}O_9$, may be obtained by the cyanide reaction, of which the one, as lactone, has the rotation, $[\alpha]_D = +45.9°$, and the other $+23.6°$ (in water, $c = 10$). In these cases, it has been well established that the configuration formulas are:

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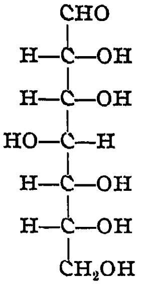
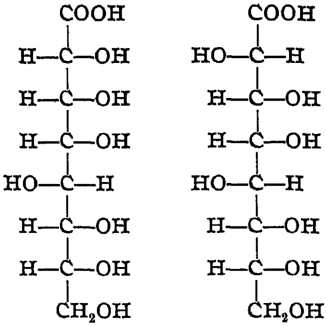
[1] Wallach: Ber. d. chem. Ges., **28**, 1308.

[2] Wallach · Ann. Chem. (Liebig), **270**, 175.

[3] Wallach : *Ibid.*, **246**, 227.


α-Glucoheptose


Glucooctonic acid.

In the same way two isomeric rhamnohexonic acids, $C_7H_{14}O_7$, whose lactones have the rotations $[\alpha]_D = +83.8°$ and $+43.3°$, are formed from rhamnose, $C_6H_{12}O_5$ (Fischer and Piloty).[2] On the contrary from mannose, $C_6H_{12}O_6$, by aid of the cyanide reaction, only one of the mannoheptonic acids, $C_7H_{14}O_8$, could be obtained; *d*-mannose furnished a left-rotating acid lactone ($[\alpha]_D = -74.2°$), *l*-mannose a right-rotating ($[\alpha]_D = +75.2°$). The two corresponding antipodes were therefore formed which united to produce a crystalline compound. This case shows that the formation of one of the two possible isomers may be particularly favored (Fischer,[3] Smith,[4] Hartmann).[5]

c. Increase of the number of asymmetric carbon atoms takes place also by the combination of active bases with active acids, in which case two pairs of antipodes with different properties must result. Of salts of this kind, the following have been made·

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[1] Fischer Ann Chem (Liebig), **270**, 64

[2] Fischer and Piloty Ber d chem Ges, **23**, 3104

[3] Fischer and Hirschberger. *Ibid.*, **22**, 370, Fischer and Passmore *Ibid*, **23**, 2226

[4] Smith Ann. Chem (Liebig), **272**, 182.

[5] Hartmann *Ibid.*, **272**, 190.

Marckwald[1] has combined *d*- and *l*-α-pipecoline with *d*- and *l*-tartaric acid, forming acid tartrates, the water of crystallization, melting-points, and crystalline forms of which he determined. He did the same with the salts from racemic acids and bases. The results were

				Melting-point	
		Water of crystallization.	Crystalline form	Hydrated salt	Anhydrous salt
+ Tartaric acid	+ pipecoline	2 mol.	monoclinic hemimorphous enantiomorphous	65–66°	111–112°
— "	— "				
+ "	— "	1 "	?	45–46°	126°
— "	+ "				—
r- "	*r*- "	1 "	monoclinic	85°	—

The acid tartrates of d- and l-limonene-α-nitrolbenzylamine, $C_{10}H_{16}.NO.NH\ CH_2C_6H_5$, were examined by Wallach and Conrady[2] with respect to their rotation. The solutions in aqueous alcohol contained 0.97 to 1 38 per cent of salt

$$\left\{\begin{array}{l}+\text{ tartaric acid }+\text{ base, }[\alpha]_D=-49\ 9^\circ\\ -\quad\text{"}\quad -\quad\text{"}\quad\text{"}=+51.0^\circ\end{array}\right.$$
$$\left\{\begin{array}{l}+\quad\text{"}\quad -\quad\text{"}\quad\text{"}=+69\ 6^\circ\\ -\quad\text{"}\quad +\quad\text{"}\quad\text{"}=-69\ 9^\circ\end{array}\right.$$

From this the rotations follow :

+ base = − 60° + acid = + 10°
— " = + 60 — " = − 10°

In the two bases a change of rotation follows on combination with tartaric acid.

The following observations have been made by Fileti[3] on salts of *d*- and *l*-isopropylphenylglycolic acid ($[\alpha]_D = \pm 135^\circ$) with quinine and cinchonine :

		Melting-point	$[\alpha]_D$
+ Isopropylphenylglycolic acid	— quinine,	192–193°	— 79.4°
— " " " "	— "	204–205	— 118.4
+ " " " "	+ cinchonine	201	+ 136.8
— " " " "	+ "	167	+ 83.4

From this the differences in the two not-antipodic isomers are apparent.

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[1] Marckwald ; Ber. d. chem. Ges., **29**, 43.

[2] Wallach and Conrady · Ann. Chem. (Liebig), **252**, 148.

[3] Fileti : Gazz. chim. ital., **22**, II, 395 ; Ber. d. chem. Ges., **26**, IV, 89.

37.—3. Formation of Active Bodies in the Animal or Vegetable Cell. —In the production of asymmetric bodies in the vegetable cell from inactive materials, it might be expected, as in artificial syntheses, that the two antipodes would be formed and racemic bodies result. Secondly, it might be possible that of the different configurations of a molecule, several, or indeed all might be formed at the same time. As far as experience has shown, up to the present time, however, of such possible plant isomers, only one is produced, and this generally one of the active forms. Of the hexoses only the right-rotating *d*-glucose, of the ketoses, only the left-rotating *d*-fructose appears (E Fischer),[1] of the four tartaric acids, only the active right-rotating form The same thing is seen in whole groups of vegetable substances, such as the bitter principles and alkaloids, which have all been found in one of the two active forms only In the turpentine oils from the different species of pine, as well as in other ethereal oils there is found either *d*-pinene and *d*-limonene, or, on the other hand, *l*-pinene and *l*-limonene , but at the same time dipentene may also be contained in them, and we have here a case of the formation of a racemic body in the plant

A suggestion of the manner in which new active bodies may be made from others already present in the plant-cell has been given by E Fischer[2] This is based on the fact that in the artificial building up of sugars from others of a smaller number of carbon atoms by aid of the cyanhydrin reaction, the once existing asymmetry of the molecule is further continued. Imagine, for example, the conversion of mannose by the addition of cyanhydric acid three times into mannononose, and this then so split up that the original hexose would be reproduced, then the second compound with three carbon atoms would be also an active system ; the first active molecule has produced a second one. In the same manner from the active substances in the chlorophyl grains, which are held by vegetable physiologists to be the seat of the formation of sugar, this latter body could be formed by the taking up of carbonic acid or formaldehyde, condensation, and final splitting off. As sugar, in turn, is used by the plant in the formation of other organic substances, these furnish the material for the production of new chlorophyl grains which again build up sugar, and thus, a direct and continuous creation of asymmetric molecules takes place. Similar views have been expressed by Stohmann.[1]

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[1] E Fischer : Ber. d. chem Ges., 27, 3230.

[2] E Fischer *Ibid* , 27, 3231.

In what manner the first active substance is formed in the plant-cell can not, of course, be explained, nor also, the reason why in one body the formation of a right-rotating and in another, of a left-rotating modification is preferred. The assumption that both forms are simultaneously produced and one immediately destroyed, that is, used to build up other substances, appears untenable, as the last process could not take place momentarily, and racemic bodies should then be found in part in plants, which, as remarked above, is very seldom the case.

In the animal organism which is formed mainly of asymmetric substances, and receives such as food, the production of new active compounds by addition and decomposition can follow. With this, there is the possibility that inactive bodies present may take part in the changes, and so be converted into active substances This is shown, for example, by the observation that brombenzene taken into the organism appears in the urine as active bromphenylmercapturic acid.[2]

It is remarkable that the proteid bodies of the animal kingdom, and also of the vegetable, show, without exception, left rotation. On the other hand, the bile acids nearly all rotate to the right.

F. Transformation of the Active Isomers

38. Reciprocal Transformation of the Antipodes.—A general method by which active bodies may be half converted into oppositely rotating antipodes consists in converting them into racemic forms and splitting these. In this way Lewkowitsch[3] obtained from *l*-mandelic acid the *d*-acid. Piutti[4] by treating

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[1] Stohmann Ztschr f Biologie, Jahrg., 1894.

[2] Jaffé Ber d. chem. Ges, 12, 1092 · Baumann and Preusse: Ztschr. physiol. Chem., 5, 309; Baumann · Ber. d. chem. Ges., 15, 1731.

[3] Lewkowitsch: Ber. d. chem. Ges, 16, 2722.

[4] Piutti Gaz. chim ital, 17, 126; Jahresbericht, (1887), 1664.

d-asparagine with alcohol and hydrochloric acid obtained the racemic monoethyl ester of aspartic acid, from which by treatment with ammonia he obtained asparagine again in the racemic form, and this was finally split by crystallization. This method, however, has but a limited application because with a large number of substances racemization can be brought about with difficulty or not at all.

A quite distinct process for the transformation of the antipodes was applied by Walden[1] in the case of malic acid. By treating the common *l*-acid ($[\alpha]_D = -5^\circ$ to $5\ 3^\circ$ in acetone, $c = 13$ to 16) with phosphorus pentachloride with addition of chloroform, thus avoiding high temperature, active monochlorsuccinic acid results and in the right-rotating form. By now replacing the chlorine in this by hydroxyl (by boiling the aqueous solution, neutralized with potassium carbonate, with silver nitrate) malic acid results, and this rotates just as much to the right as the original acid did to the left. On the other hand, the *d*-acid so obtained yields *l*-monochlorsuccinic acid on treatment with phosphorus pentachloride and from this *l*-malic acid may be reproduced We have thus a perfect cycle of changes The conversion of either of the two malic acids into the other may be brought about by converting the corresponding dimethyl ester, which has the same rotation into the dimethyl chlorsuccinic ester by aid of phosphorus pentachloride, and in this conversion the direction of rotation changes

An explanation of the peculiar change in rotation and molecular configuration which follows in the substitution of hydroxyl by chlorine under the action of PCl_5 has been attempted by Armstrong[2]

Of a different kind are a number of observed changes of active bodies into oppositely rotating isomers, inasmuch as the latter are not the true antipodes of the original substances, which follows from the fact that racemic compounds do not result as end products. The inversion of *l*-menthone into *d*-menthone, or the reverse, which follows by the action of weak or strong sulphuric acid, hydrochloric acid or alcoholic potash, and which was discovered by Beckmann[1] is a case in point. In the same way *l*-ecgonine and *l*-cocaine may be converted by heating into right-rotating isomers (Einhorn and Marquardt).[2]

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[1] Walden· Ber d chem Ges , 29, 153.

[2] Armstrong Proceedings Chem Soc , (1896), page 45. On the change of *d*-lactic acid into *l*-lactic acid, see Purdie and Williamson : J Chem Soc., 69, 837.

See further the chapter on the direction of rotation of the derivatives of active bodies

39. **Reciprocal Transformation of Active Isomers of Different Configurations.**—Such changes were discovered, as is known, by E. Fischer,[3] and especially in the acids of the sugar group. They occur when these acids are heated with quinoline or pyridine to 130°–150°, in which the addition of the bases is employed mainly to prevent the production of lactones which interfere with the reaction. According to experience up to the present, a change of position of the H and OH on the asymmetric carbon attached to the carboxyl group follows, and this reaction appears to be always reversible, so that the product is a mixture of the original acid with the one newly formed. Thus, the following stereoisomeric acids have been reciprocally converted, the one into the other.[4]

$C_5H_{10}O_6$	*l*-Arabonic acid $A\ \begin{smallmatrix}\times&\times&\bullet\\ \bullet&\bullet&\times\end{smallmatrix}\ X$	$\rightleftarrows$	*l*-Ribonic acid $A\ \begin{smallmatrix}\times&\times&\times\\ \bullet&\bullet&\bullet\end{smallmatrix}\ X$
$C_6H_{12}O_7$	*d*-Gluconic acid $A\ \begin{smallmatrix}\bullet&\bullet&\times&\bullet\\ \times&\times&\bullet&\times\end{smallmatrix}\ X$	$\rightleftarrows$	*d*-Mannonic acid $A\ \begin{smallmatrix}\bullet&\bullet&\times&\times\\ \times&\times&\bullet&\bullet\end{smallmatrix}\ X$
	l-Gluconic acid $A\ \begin{smallmatrix}\times&\times&\bullet&\times\\ \bullet&\bullet&\times&\bullet\end{smallmatrix}\ X$	$\rightleftarrows$	*l*-Mannonic acid $A\ \begin{smallmatrix}\times&\times&\bullet&\bullet\\ \bullet&\bullet&\times&\times\end{smallmatrix}\ X$
	d-Galactonic acid $A\ \begin{smallmatrix}\bullet&\times&\times&\bullet\\ \times&\bullet&\bullet&\times\end{smallmatrix}\ X$	$\rightleftarrows$	*d*-Talonic acid $A\ \begin{smallmatrix}\bullet&\times&\times&\times\\ \times&\bullet&\bullet&\bullet\end{smallmatrix}\ X$
	l-Gulonic acid $A\ \begin{smallmatrix}\bullet&\times&\bullet&\bullet\\ \times&\bullet&\times&\times\end{smallmatrix}\ X$	$\rightleftarrows$	*l*-Idonic acid $A\ \begin{smallmatrix}\bullet&\times&\bullet&\times\\ \times&\bullet&\times&\bullet\end{smallmatrix}\ X$

Besides these cases others are known

G. Inseparable Modifications of Inactive Configuration

40. As already explained in the chapter on the number of isomers possible in bodies with asymmetric carbon atoms (§ 16)

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[1] Beckmann· Ann. Chem. (Liebig), **250**, 342, **289**, 362.

[2] Einhorn and Marquardt: Ber. d. chem Ges, **23**, 468, 979.

[3] E Fischer. *Ibid.*, **23**, 799; **24**, 2137, 3622; **27**, 3193.

[4] In the formulas $A = CH_2OH$, $X = CO_2H$, $\bullet = H$, $\times = OH$.

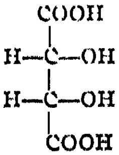
this type may appear in such molecules whose formulas may be divided into two equal halves. The inactivity may be explained by the equally strong but oppositely directed rotating power of the two halves which compensate each other.

The correctness of this view follows from the fact that when the symmetry of such a molecule is destroyed, an active product results. This was shown first by E. Fischer.[1] As he found, the inactive mucic acid, $CO_2H—(CHOH)_4—CO_2H$, yields by reduction racemic galactonic acid, $CHO—(CHOH)_4—CO_2H$, which may be split into active components, and conversely these, as well as the galactoses, may be converted by oxidation into inactive non-separable mucic acids.

Inactive isomers of this kind are found in the following classes of symmetric bodies:

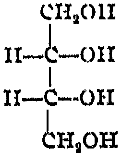
1. In chain structure compounds with an even number of carbon atoms.—In this case, according to § 16, the number, i, of inactive modifications is given by the formula, $i = 2^{\frac{n}{2} - 1}$, where n is the whole number of asymmetric carbon atoms. The bodies of this group which are known are mainly these:

Among those with $n = 2$, where $i = 1$, there is, first of all, the meso- or antitartaric acid discovered by Pasteur[2] in 1853, in which the impossibility of resolution and consequent difference from racemic acid (paratartaric acid) was shown. The configuration of this, as also that of erythritol, whose inactivity has also been shown, must be given, according to §16, by



$$\begin{array}{c} COOH \\ | \\ H—C—OH \\ | \\ H—C—OH \\ | \\ COOH \end{array}$$

Mesotartaric acid.



$$\begin{array}{c} CH_2OH \\ | \\ H—C—OH \\ | \\ H—C—OH \\ | \\ CH_2OH \end{array}$$

Erythritol.

A further number of such symmetric bodies as the di- and tetrasubstituted succinic acids, also erythritol derivatives, hydrobenzoin, etc., are undoubtedly likewise inactive.

Among compounds with $n = 4$, and consequently $i = 2$, we have:

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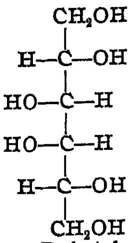
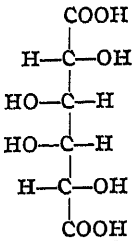
[1] E. Fischer: Ber. d. chem. Ges., 25, 1247, 1260.

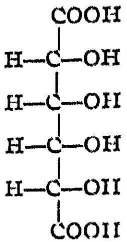
[2] Pasteur: Compt. rend., 37, 162. See Przybytek: Ber. d. chem. Ges., 17, 1415.



Dulcitol.



Mucic acid



Allomucic acid.

With the octitols and their corresponding acids, four isomers with inactive configuration are possible, but we are not yet acquainted with them.

Naturally no change follows in the above relations, if an even number of carbon atoms with two similar radicals attached (CH_2 groups) are introduced into the middle of the molecule, as is the case with .

Dimethyladipic acids,
$(CO_2H—{}^*CH\ CH_3)—CH_2—CH_2—({}^*CH.CH_3—CO_2H)$
Diallyl bromides, $(CH_2Br—{}^*CHBr)—CH_2—CH_2—({}^*CHBr—CH_2Br)$

and others

2 *In chain-structure compounds with an uneven number of carbon atoms.*—Here the number of possible isomers is dependent on the form of combination of the radicals with the middle carbon atom

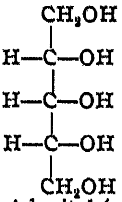
a If the middle carbon atom besides being united with the two symmetric groups is joined to two other radicals, similar to each other, as in the α-dimethylglutaric acids,

$$(CO_2H—{}^*CH.CH_3)—CH_2—({}^*CH.CH_3—CO_2H),$$

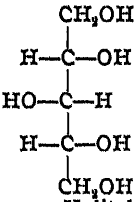
then the number of inactive isomers may be calculated by the formula used for the bodies of the last group.

b. If, on the other hand, the middle carbon atom, besides being attached to the symmetric groups, is joined to two other dissimilar radicals, then the number of inactive isomers may be found by the formula, $z = 2^{\frac{n-1}{2}}$, where n is the number of asymmetric carbon atoms, *the middle carbon atom being included as one* In reality, however, this atom should not be considered as asymmetric, because, as a glance at the following configuration formulas will show, a plane of symmetry may be passed through the same, and the dissimilar radicals joined to it. If this middle carbon atom is excluded, the number of inactive isomers is given by the formula, $i = 2^{\frac{n}{2}}$

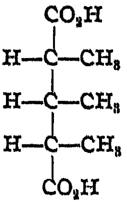
The following are bodies of this class:

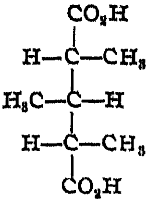


Adonitol (ribitol).
Ribotrioxylglutaric acid.



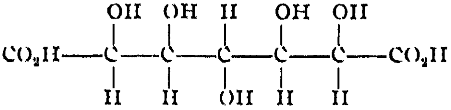
Xylitol.
Xylotrioxyglutaric acid





Trimethylglutaric acids.

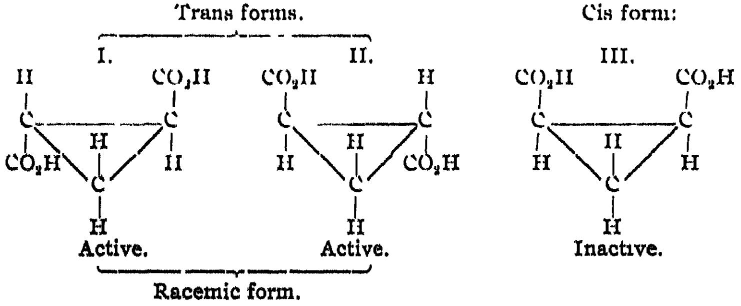
Bodies which contain five, or according to the above considerations four, asymmetric carbon atoms, furnish four inactive isomers of which at present α-glucoheptonpentoldiacid,



$$CO_2H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CO_2H$$

and α-glucoheptitol are known.

3. *In cis-form cyclic compounds.* The simplest case is given by the 1,2-trimethylenedicarboxylic acids, where, as is known, three isomers are possible:



The asymmetric symbols, I and II, which stand in the relation of object and image to each other, correspond to the active forms, while the third symbol possesses a plane of symmetry, passing through the group CH_2, and therefore represents an inactive type. In an analogous way are related the hexahydrophthalic acids, the hexahydroisophthalic acids, the Δ^1-tetrahydroterephthalic acids, and others, in which the racemic modification (trans form) and the structurally inactive (cis) form are known.

41. Differences in the Properties of Racemically Inactive and Structurally Inactive Isomers.—These have been observed with respect to

a Water of Crystallization.—For example:

Calcium mesotartrate.... ..$CaC_4H_4O_6 + 3\,CH_2O$ (Anschütz)[1]
Calcium racemate....... ..$CaC_4H_4O_6 + 4H_2O$
Calcium *d*- and *l*-tartrate....$CaC_4H_4O_6 + 4H_2O$

Free mesotartaric acid, like racemic acid, crystallizes with one molecule of water; the inactive tartaric acids, on the contrary, are anhydrous.

b. Melting-Point.—As may be seen from the following observations, the melting-point of the racemic modification is generally higher than that of the inactive modification, although the reverse relation also appears In the last cases, however, including erythritol and some of its derivatives, it is possible that mixtures, rather than racemic compounds, were examined:

	Racemically inactive	Configurationally inactive.	Diff $R—C$	Observer
Racemic or tartaric acid, anhyd.	205–206°	140–143°	+ 64°	Bisch. and W [2]
Dimethylsuccinic acid	194	120	+ 74	Walden[3]
Diethylsuccinic acid...... .	192	128	+ 64	“
Diphenylsuccinic acid...........	229	183(220)	+ 46(9)	“
Dimethylglutaric acid	122–127	99–101	+ 24.5	“ [3]
Erythritol.....	72	118	— 46	Griner[4]
Erythritoldibromhydrine	83	135	— 52	“ [5]
Erythritoldibromacetine	96	133–134	— 37.5	“
1,2-Trimethylenedicarboxylic acid	175	139	+ 36	Buchner[6]
Hexahydrophthalic acid	215	192	+ 23	v. Baeyer[7]
Hexahydroisophthalic acid	118–120	161–163	— 43	Perkin[8]
Δ^2-Tetrahydroterephthalic acid.	220	150–155	+ 67	v. Baeyer[9]

[1] Anschütz Ann Chem. (Liebig), **226**, 197
[2] Bischoff and Walden Ber d chem Ges., **22**, 1815.
[3] Walden Ztschr phys Chem, **8**, 467.
[4] *Ibid*, p. 487
[5] Griner Compt rend, **116**, 723, **117**, 553.
[6] Buchner Ber d chem Ges, **23**, 703.
[7] v Baeyer · Ann Chem (Liebig), **258**, 218
[8] Perkin, J Chem Soc, **59**, 813
[9] v Baeyer: Ann Chem (Liebig), **251**, 308

c. Solubility.—In the cases which have been studied, the compounds inactive by configuration have been always more readily soluble than the racemic forms. One hundred parts of water dissolve:

	Racemically inactive.	Configurationally inactive	Active	Observer
Tartaric acids, anhydrous at 15°	17.1 pts.	125.0 pts.	132.2 pts.	Bischoff&
Acid potassium tartrate at 19° ...	0.555 "	12.5 "	0.535 "	Walden[1]
Δ^2Tetrahydroterephthalic acid } cold water.	0.170 "	2.70 "	—	v. Baeyer[2]

d. Constant of Dissociation, K, determined from electrical conductivity. The following observations exhibit no regularity in this relation:

	Racemically inactive	Configurationally inactive	Diff *R—C*	Observer
Racemic acid, mesotartaric acid,	0.097	0.060	+ 0.037	Walden[3]
Dimethylsuccinic acid	0.0191	0.0123	+ 0.0068	" [4]
Diethylsuccinic acid	0.0245	0.0343	— 0.0098	"
Diphenylsuccinic acid.. ..	0.020	0.026	— 0.006	"
Dimethylglutaric acid ...	0.0055	0.0055	0	" [5]

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[1] Bischoff and Walden Ber d chem Ges, **22**, 1817

[2] v Baeyer Ann Chem (Liebig), **251**, 307

[3] Walden Ber d chem Ges, **22**, 1820, Ostwald Ztschr phys Chem, **3**, 372, Berthelot Ann chim phys [6], **23**, 90

[4] Walden Ztschr phys Chem, **8**, 467

[5] Walden *loc cit*, p 487

PART SECOND

Physical Laws of Circular Polarization

FUNDAMENTAL RELATIONS

With one and the same active body, the angle through which the plane of transmitted polarized light is rotated, depends on the following three factors :

1. On the length of column.
2. On the wave length of the light ray.
3. On the temperature of the active substance.

42. Relation of Rotation to Length of Column.—Observations carried out by Biot[1] in 1817 led to the following empirical rules which hold strictly true for solid as well as liquid active bodies :

1. The angle through which the plane of polarization of a ray of given wave length is rotated is proportional to the length of the active column

2. If the ray is allowed to pass through a number of separate layers, the final deviation of the plane is equal to the sum of the single deviations if the layers or columns all rotate in the same direction, or equal to their differences in case they possess opposite rotating powers.

In comparing the rotations of different active substances it is customary, according to Biot's suggestion, to reduce the angle of rotation of solid bodies to that of a plate of 1 mm. thickness and of liquids to that of a column 1 dm. in length.

43. Dependence of the Angle of Rotation upon the Wave-Length of the Ray. Rotation Dispersion.—The rotation of the plane of polarization experienced by rays of different colors in passing through an active layer is least for red and greatest for violet light ; it increases, therefore, with decrease in the wave-length of the light. Biot drew the conclusion from his measurements on quartz plates that the angle of rotation, α, is inversely proportional to the square of the wave-length, λ; but later observation showed that this rule is only approximately true. A formula of the form $\alpha = A + \frac{B}{\lambda^2}$, with the constants A and B, is likewise inadequate to express the relation exactly, but Boltzmann[1] has shown that the formula

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[1] Biot Mém. de l' Acad , 2, 41, 91 (1817). Ann chim. phys [2], 10, 63 (1819)

$$\text{(I)} \qquad \alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^4}$$

corresponds to the observations in a satisfactory manner. The law of rotation dispersion is still better given in a theoretically derived formula by E. Lommel,[2] which contains the two constants, a and λ_0^2:

$$\text{(II)} \qquad \alpha = \frac{a}{\lambda^2\left(1 - \frac{\lambda_0^2}{\lambda^2}\right)^2}.$$

In order to determine the constants of both expressions for a given substance, the angles of rotation, $\alpha_1, \alpha_2, \alpha_3, \ldots$ observed for a number of rays of known wave-length, $\lambda_1, \lambda_2, \lambda_3 \ldots$ must be found by measurements A and B may then be calculated from each pair of exact observations,[3] and finally from the results of all the possible combinations, the mean may be taken, or the method of least squares may be applied. In order to obtain convenient numerical values, the wave-lengths are best expressed in millimeters, for example, $\lambda = 0.0006562$.

The formulas (I) and (II) may be employed also to determine the wave-length of any kind of light by measuring the

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[1] Boltzmann: Pogg. Ann., Jubelb. (1874), p. 128.

[2] E. Lommel: Theorie der Drehung der Polarisationsebene, Wied. Ann., 14, 523 (1881); Das Gesetz der Rotations dispersion, Wied. Ann., 20, 579 (1883).

[3] From the Boltzmann equations.

$$\alpha_{\text{I}} = \frac{A}{\lambda_{\text{I}}^2} + \frac{B}{\lambda_{\text{I}}^4} \quad \text{and} \quad \alpha_{\text{II}} = \frac{A}{\lambda_{\text{II}}^2} + \frac{B}{\lambda_{\text{II}}^4};$$

there follow:

$$A = \frac{\frac{\alpha_{\text{I}}}{\lambda_{\text{II}}^4} - \frac{\alpha_{\text{II}}}{\lambda_{\text{I}}^4}}{\frac{1}{\lambda_{\text{I}}^2\lambda_{\text{II}}^4} - \frac{1}{\lambda_{\text{II}}^2\lambda_{\text{I}}^4}} \quad \text{and} \quad B = \frac{\frac{\alpha}{\lambda_{\text{II}}^2} - \frac{\alpha_{\text{II}}}{\lambda_{\text{I}}^2}}{\frac{1}{\lambda_{\text{II}}^2\lambda_{\text{I}}^4} - \frac{1}{\lambda_{\text{I}}^2\lambda_{\text{II}}^4}}$$

angle of rotation produced in it by any substance, the rotation dispersion of which is known; for example, quartz. If we apply the Boltzmann formula, $\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^4}$, and take

$$\frac{A}{\alpha} = a \quad \text{and} \quad \frac{B}{\alpha} = b,$$

we have next to determine the value,

$$\frac{a}{2} + \sqrt{\frac{a^2}{4} + b} = c$$

from which the desired wave-length, expressed in millionths of a millimeter ($\mu\mu$), is given by

$$\lambda = 10^3 \sqrt{c},$$

if the millimeter scale wave-lengths are used in calculating A and B.

From the Lommel formula there follows:

$$\lambda^2 = \frac{A}{2\alpha} - B + \sqrt{\frac{A^2}{4\alpha^2} - \frac{AB}{\alpha}}.$$

The methods by which the angles of rotation for a number of rays of known wave-length were measured and from this the rotation dispersion of a substance determined are described in Part IV. Observations thus far carried out are based either on the Fraunhofer sun lines or on the lithium, thallium, or sodium line, or finally on certain kinds of approximately monochromatic light obtained by so-called ray filters. Up to the present time exact data have been given mainly for the following substances:

44. **Rotation Dispersion of Crystals.** 1. *Quartz.*—Several series of observations on this substance are on record, among which the older ones by Broch[1] (1852), Stefan[2] (1864), Soret and Sarasin[3] (1876), may be excluded as the influence of temperature was not sufficiently considered, in reference to which it was first shown by Dubrunfaut[4] and later by v. Lang[5] that it exercises a not unimportant effect on the rotating power of quartz. Soret

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[1] Broch Dove's Repert d Phys., **7**, 115, Ann. chim. phys. [3], **34**, 119 (1852).

[2] Stefan Wien Ber , **50**, II.; Pogg. Ann., **122**, 631, 1864.

[3] Soret and Sarasin· Pogg Ann , **157**, 447 (1876).

[4] Dubrunfaut Compt. rend , **23**, 44 (1846)

[5] v Lang Wien. Ber , **71**, II, 707 (1875). Pogg Ann., **156**, 422 (1875).

and Sarasin[1] then published two new series of observations which are based accurately on a temperature of 20°, and which may now be looked upon as the most reliable. These observations cover 29 lines, from wave-length 214–760 $\mu\mu$; those referring to the visible lines from *A* to *H* are given in the table below. A quartz plate having a thickness of 30 mm. was used in the observations under I, while a plate with a thickness of 60 mm. served for the observations under II. Some exact observations by V. v. Lang are given also.[2]

QUARTZ. ANGLE OF ROTATION FOR 1 MM.

Fraunhofer lines.	Wave-lengths according to Angström λ in $\mu\mu$.	Observed by Soret and Sarasin. Temperature 20°. I	II.	Mean.	Calculated by the formula of Lommel.
A	760.4	12.668°[3]	12 628°[1]	12 65°	12.78°
a	718.36	14 304	14 298	14.30	14.37
B	686.71	15 746	......	15 75	15.78
C	656 21	17.318	17.307	17.31	17.34
D_2	589.513	21.684	21.696	21 69	21.70
D_1	588.912	21.727	21.724	21.725	21.74
E	526 913	27 543	27.537	27.54	27.51
F	486.074	32 773	32 749	32.76	32.69
G	430.725	42.604[3]	42.568[3]	42.59	42.51
h	410.12	47.481	47.492	47.49	47.36
H	396.81	51.193[3]	51.182[3]	51.19	50.97

Lines.	λ	v Lang Temp 21°.	Rays.	λ	v Lang Temp 0°	v Lang Temp 20°.
C	656.21	17.299°	*Li*	670.8	16.402°	16.460°
D	589.21	21.727	*Na*	589.2	21.597	21.660
F	486.07	32.722	*Tl*	535.1[4]	26.533	26.611[5]

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[1] Soret and Sarasin: Compt. rend., 95, 635 (1882); Arch de Genève, 8, 5, 97, 201.

[2] V. v. Lang: Wien. Ber., 74, II., 209 (1876).

Further measurements have been made by Wasastjerna (Wied. Beibl., 15, 111 (1891)) but the temperatures are not given. The rotation of infra red rays in quartz has been investigated by P. Desains (Compt. rend., 84, 1056 (1877)); Hussel (Wied. Ann., 43, 498 (1891)) and Carvallo (Compt. rend., 114, 288; Ann. chim. phys. [6], 26, 13 (1892)). The observations of Soret and Sarasin extend to the ultraviolet rays.

[3] Observations of less certainty.

[4] According to Kayser (Landolt-Börnstein, Phys. chem. Tab., p. 383).

[5] Calculated from the data for 0° by means of Gumlich's temperature formula.

The observations of Soret and Sarasin may be expressed by the Boltzmann dispersion formula with the constants:

$$\alpha = \frac{7.108\,2930}{10^6 . \lambda^2} + \frac{0.147\,7086}{10^{12} . \lambda^4},$$

(λ in millimeters)

and also by the formula of Lommel:

$$\alpha = \frac{a}{\lambda^2 \left(1 - \frac{\lambda_0^2}{\lambda^2}\right)^2}$$

in which

$$\log a = 0.855\,5912, \log \lambda_0^2 = 7.935\,1257 - 10.$$

(λ in thousandths of a millimeter μ)

The angles of rotation calculated in this way are given in the last table

Rotation of Quartz for Sodium Light [1]—Among observations in this direction, those recently carried out by Gumlich[2] in the physikalisch-technischen Reichsanstalt must be considered the most accurate. In these investigations, about twelve right- and left-rotating round quartz plates, 50 to 60 mm. in diameter, from 1.2 to 10.5 mm. in thickness (measured to 0.1 μ), and, as nearly as possible, with plane parallel surfaces (maximum difference in thickness 0.5μ) were used. They were ground perpendicularly to the optical axis as perfectly as possible, and special measurements showed that the axis error, that is, the angle between the optical axis and normal to the plate surface, was never more than 16′. The sodium light employed (from sticks of soda in oxyhydrogen lamp) passed first through prisms[3] and a slit, the latter of which served to cut out foreign rays. The determination of the angle of rotation was made by aid of a Lippich half-shadow apparatus and in order to eliminate the error from lack of perfect parallelism in the plates, the latter were adjusted in four positions, 90° apart. To determine the effect of temperature, the measurements were made in a room, the temperature of which could be varied between 0° and 30°. The investigations led to the following results:

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[1] See later, Part IV.

[2] E Gumlich: Wissenschaftl. Abhandlungen der Physikalisch-technischen Reichsanstalt, 2, 201 (1895), Ztschr für Instrumentenkunde, 1896, p. 97.

[3] Two Wernicke hollow prisms containing ethyl cinnamate.

Pure sodium light is rotated by a quartz plate, 1 mm. in thickness at a temperature of 20°,

$$21.7182° \pm 0.0005,$$

provided the light passes through the plate exactly in the direction of the optical axis. Under other conditions the rotation is somewhat larger, when the plates were set exactly perpendicular to the entering light, the angle was, on account of the axis error, in the mean 21.7223° ±0.0010.

The angles of rotation for right- and left-handed plates were found to be exactly the same, and it was further found that quartzes from different localities (Brazil, Japan, Switzerland) showed no appreciable variations.

A difference in the behavior of unequally intense lights (oxyhydrogen lamp, Landolt lamp) could not be recognized with certainty when the purification of the light from foreign rays was effected by the spectrum method But when this was done by other methods (Lippich's ray filter with potassium dichromate and uranous sulphate) appreciable differences appeared

Other observers have found earlier the following figures as expressing the rotation of quartz for sodium light at 20° [1]

Broch (1846)	21.67	v Lang (1876)	21.724.
Stefan (1864)	21 67.	Joubert (1878)	21 723
Wild (1864)	21.67	Soret and Sarasin (1882)	21.723
Mascart (1872)	21 746	Soret and Guye (1892/3)	21 718 and 729
v Lang (1875)	21.661.		

Effect of Temperature on the Rotating Power of Quartz — This is exerted, as first shown by v. Lang,[2] in the sense that with an increase of temperature, an increase in the rotation follows. The increase may be expressed by the following formulas in which α_t represents the angle at a higher temperature, and α_0 that at a lower temperature.

Within mean temperatures Gumlich[3] found for right- and left-rotating quartz and sodium light:

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[1] See Gumlich: *Loc. cit.*, p. 246.

[2] v Lang Pogg Ann., 156, 422 (1875).

[3] Gumlich. *Loc cit*, p 230

$$\alpha_t = \alpha_0\ (1 + 0\ 0_3144\ t + 0\ 0_6146\ t_2)$$

and for smaller differences in temperature

$$\alpha_t = \alpha_0\ (1 + 0.0_3147\ t)$$

holding between 0° and 30°

Other observers have given coefficients which agree with this, thus

v. Lang,[1] $\alpha_t = \alpha_0\ (1 + 0\ 0_3149\ t)$, holding between 20° and 100°,
Sohncke,[2] $\alpha_t = \alpha_0\ (1 + 0.0_3148\ t)$, " " 23° " 100°,
Joubert,[3] $\alpha_t = \alpha_0\ (1 + 0\ 0_3149\ t)$, " " 0° " 100°,
" $\alpha_t = \alpha_0\ (1 + 0\ 0_31463\ t + 0.0_7329\ t^2)$ —20° " 100°.

For low temperatures, Soret and Guye[4] found :

$\alpha_t + \alpha_0\ (1 + 0.0_31326\ t)$, holding between —55° and +23°,
$\alpha_t + \alpha_0\ (1 + 0.0_31265\ t)$, " " —72° " +18°.

According to Le Chatelier[5] the rotation increases irregularly at high temperatures Based on observations made by him, that quartz undergoes a sudden change in dimensions at 570°, he calculates the following formulas:

Between 0° and 570° ·

$$\alpha_t = \alpha_0\ (1 + 0\ 0_496\ t + 0.0_6217\ t^2)$$

At 570° there is an increase, $\Delta\ \alpha = 0.043\ \alpha_0$.

Above 570° this expression holds .[6]

$$\alpha_t = \alpha_0\ (1.165 + 0.0_415\ (t - 570^\circ))$$

The angles of rotation found by Le Chatelier are ·

t	Diff	$\lambda = 656 = C$	$\lambda = 589 = D$	$\lambda = 518$	$\lambda = 500$	$\lambda = 448$ μμ *Mg-line*
20°		17 25	21 72	28 62	30.78	39.24
280	260	18 06	22.68	29 82	32 16	40.80
415	135	18 60	23.40	30 60	32 90	42 00
560	145	19 38	24 30	32 04	34.56	44.10
600	40	20 10	25.26	33.18	35 76	45.60
900	300	—	25.32	33 24	36.00	45 84

In these figures the sudden strong increase between 560° and 600° may be recognized.

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[1] v. Lang *Loc. cit*
[2] Sohncke Wied. Ann , 3, 516.
[3] Joubert Compt 'rend., 87, 497
[4] Soret and Guye. *Ibid* , 115, 1295 , 116, 75
[5] Le Chatelier · *Ibid.*, 109, 244 (1889)
[6] Confirmed by Gumlich . *Loc cit* , p 230

According to v. Lang,[1] Sohncke[2] and Le Chatelier[3] the temperature coefficient remains constant for rays of all wave-lengths, but more exact measurement would probably disclose differences here.

The rotation of quartz at low temperatures has been carefully investigated by Soret and Guye.[4] For a plate having the thickness of 1 mm. at 12° the following rotations of the sodium ray were found:

$t =$	-71.5	$-55.3°$	$-42.3°$	$0°$	$+17.7°$	$+22.7°$,
$\alpha_D =$	21.470	21.505	21.537	21.655	21.719	21.730.

These observations may be expressed with satisfactory accuracy by the interpolation formula of Joubert given above.

2. *Sodium Chlorate*, $NaClO_3$.—The angles of rotation of the regular crystals were determined by Guye[5] and also by Sohncke[6] for different rays and temperatures. Based on a thickness of 1 mm. these values were found:

Line	Guye α at 20°	Sohncke α at 21°	Guye Relation of quartz to sodium chlorate
a	2.070°	—	6.908
B	2.273	2.38°	6.927
C	2.503	2.52	6.915
D_2	3.128	D 3.16	6.9361
D_1	3.132	—	6.9362
E	3.944	3.96	6.982
F	4.670	4.61	7.013
G	6.005	5.89	7.089
h	6.675	—	7.115
H	7.174	6.86	7.134

For increase of rotation with temperature:

Guye..... $\alpha_t = \alpha_0\,(1 + 0.000586\,t)$, for $t = +\ 5$ to 28°,

Sohncke... $\alpha_t = \alpha_0\,(1 + 0.00061\,t)$, " $t = +\ 16$ " 148°.

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[1] *Loc. cit.*

[2] *Loc. cit.*

[3] *Loc. cit.*

[4] Soret and Guye: Arch. sc. phys. et. nat. Genève [3], 29, 248 (1893).

[5] Guye: Arch. de Genève, [3], 22, 130 (1889). The values for fourteen ultraviolet lines are omitted from the table.

[6] Sohncke: Wied. Ann., 3, 529 (1878).

Among other active crystals the following have been investigated with respect to their rotating power:

Sodium periodate, $NaIO_4 + 3H_2O$.
Potassium dithionate, $K_2S_2O_6$.
Lead dithionate, $PbS_2O_6 + 4H_2O$.

The data for these have already been given in § 6.

45. **Rotation Dispersion of Liquid and Dissolved Substances.**—As yet there are but relatively few observations on record in this direction, of which the older ones (on cane sugar, santonin, turpentine, bile acids, etc.) were made by the Broch method[1] and are based on the Fraunhofer lines, while the later observations have been made by the ray filter method.[1] The numerical data will be found in part VI, "Constants of Rotation."

With substances which are in themselves liquid the rotation, as far as is known, shows a normal behavior; that is, the amount of rotation increases with the refrangibility of the light. This is the case with the terpenes and also in a series of derivatives of amyl alcohol, lately studied by Guye and Jordan,[2] which all have the simple molecular weight.[3] These bodies possess very different dispersive powers, which for each substance is a characteristic constant and may be expressed by the difference $[\alpha]_{\text{violet}} - [\alpha]_{\text{red}}$, and designated as the *specific rotation dispersion*.

The same normal behavior is observed with many substances in solution (cane sugar, dextrose, santonin and derivatives, bile acids and others).

The following table will serve for the comparison of the dispersive powers of different substances with each other, and also with that of quartz, the figures referring to the rotations for the lines, B, C, D, E, F and G:[4]

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[1] See Part IV Determination of Rotation Dispersion.

[2] Guye and Jordan· Compt. rend., **122**, 883 (1896).

[3] Ramsay and Shields Ztschr. phys. Chem., **12**, 433.

[4] Cane sugar in water, $p = 10$ to 30. Stefan: Wien. Sitzber, **52**, II, 486. Cholalic acid in alcohol, $c = 3$. Hoppe-Seyler: J. prakt. Chem., [1], **89**, 257. Cholesterol in petroleum, $c = 10$ Lindenmeyer· J. prakt Chem., [1], **90**, 323. Turpentine oil and lemon oil, G Wiedemann Pogg. Ann., **82**, 222. Santonin in chloroform, $c = 3$ to 90. Nasini Accad d Lincei, [3], **13**, (1882).

				B	*C*	*D*	*E*	*F*	*G*
Quartz.........	α	1 mm	±	15.75	17.31	21.71	27.54	32.76	42.59
Cane-sugar.....	[α]	1 dm	+	47.56	52.70	66.41	84.56	101.18	131.96
Cholalic acid...	[α]	"	+	28.2	30.1	33.9	44.7	52.7	67.7
Cholesterol	[α]	"	—	20.63	25.54	31.59	39.91	48.65	62.37
Turpentine oil..	α	"	—	21.5	23.4	29.3	36.8	43.6	55.9
Lemon oil	α	"	+	34.0	37.9	48.5	63.3	77.5	106.0
Santonin	[α]	"	+	484.0	549.0	754.0	1088.0	1444.0	....

If we calculate from these figures how much more strongly the rays *C*, *D*, *E*, *F* and *G* are rotated than is the ray *B*, the following so-called *coefficients of dispersion* result.

	B	*C*	*D*	*E*	*F*	*G*
Quartz....................	1	1.09	1.38	1.75	2.08	2.70
Cane-sugar..................	1	1.11	1.40	1.78	2.13	2.77
Cholalic acid................	1	1.07	1.20	1.59	1.87	2.40
Cholesterol..................	1	1.24	1.53	1.93	2.36	3.02
Terpentine oil.............	1	1.09	1.36	1.71	2.03	2.60
Lemon oil.................	1	1.11	1.43	1.86	2.28	3.12
Santonin	1	1.13	1.56	2.25	2.98	

From this, it appears that the relation between quartz and cane-sugar is nearly constant, these substances having nearly the same rotation dispersion, while other bodies disperse either more or less strongly than quartz. This fact is applied in the construction of polarimeters with quartz-wedge compensation (Soleil's color saccharimeter and the Schmidt and Haensch half shadow saccharimeter), when, as is usual, white light is employed. The construction of these instruments presupposes equality in the dispersive power of the active substance investigated with that of the quartz-wedges, and, therefore, substances which depart much from this relation cannot be used or studied with them.

In studying the dispersion ratio between cane sugar and quartz some new observations of Seyffart[1] may be used which are based on the rotation of sugar solutions for seven artificial spectral lines. If, as a basis, a solution be taken which rotates the red hydrogen line (Hα) through the same angle as a quartz plate 1 mm. in thickness, that is 17.31°, then for the other colored rays the following angles are found which are given along with the angles for quartz for comparison. (For some of the last, marked with a *, the values were found from the above quoted measurements of Soret and Sarasin by aid of the Boltzmann interpolation formula.)

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[1] Seyffart: Wied Ann., 41, 113, 128 (1890).

Color	Line.	Wave-length	Angle of rotation		Difference
			Quartz	Cane-sugar	
Red…………	$H_{\alpha}(C)$	656.2μμ	17 31°	17.31°	—
Yellow………	$Na(D)$	589.2	21.72	21.78	0.06°
Green…………	Tl	535.0	26 64*	26.81	0.17
Greenish-blue …	$H_{\beta}(F)$	486 1	32 76	32.98	0.22
Blue…………	Sr	460 7	36.77*	37 18	0.41
"…………	H_{γ}	434.1	41.88*	42.44	0 56
Violet…………	Rb_{II}	420.2	45.00*	45.78	0.78

From these figures the following dispersion coefficients are calculated :

	H_{α}	Na	Tl	H_{β}	Sr	H_{γ}	Rb_{II}
Quartz……	1	1 255	1 539	1.893	2.124	2.419	2.600
Cane-sugar…	1	1.258	1.549	1.905	2 148	2 452	2.645

It is seen that the dispersive power of sugar exceeds that of quartz, but the difference is appreciable only in case of the blue and violet rays, which, on account of their low luminosity, are but little used in the quartz wedge saccharimeters.

The dependence of the specific rotation of cane-sugar on the wave-length, λ, of the light employed, may be expressed by a formula derived by Seyffart[1] from observations on a 20 per cent. solution. λ is expressed in millimeters.

$$[\alpha]\lambda = \frac{2\ 16036}{10^6.\Lambda^2} + \frac{5\ 47276}{10^{13}\ \lambda^4}$$

As examples of substances with larger dispersion, coupled with high specific rotation, we have the following santonin bodies, investigated by Nasini :[2]

Fraunhofer lines	Wave-length Angström μμ	Santonin $C_{15}H_{18}O_3$ Solution in alcohol $c = 1\ 782$ $t = 20^{\circ}$		Santonide $C_{15}H_{18}O_3$ Solution in chloroform $c = 3$ to 30 $t = 20^{\circ}$		Parasantonide $C_{15}H_{18}O_3$ Solution in chloroform $c = 3$ to 50 $t = 20^{\circ}$	
		[α]		[α]		[α]	
B	686.7	— 110 4°	1.00	+ 484°	1.00	+ 580.5°	1.00
C	656.2	118.8	1 08	549	1.13	655.6	1.13
D	589.2	161 0	1 46	754	1.56	891 7	1.54
E	526.9	222.6	2.02	1088	2.25	1264	2.18
b_1	518 3	237.1	2.15	1148	2.37	1334	2.30
F	486.1	261 7	2 37	1444	2.98	1666	2.87
e	438 3	380.0	3.44	2201	4 55	2510	4 32
g	422.6	—	—	2610	5.39	2963	5 10

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[1] Seyffart *Loc cit.*

[2] Nasini Accad d Lincei, Cl. sc. fis mat e. nat, [3], **13**, 1882.

If an active body is dissolved in different liquids, the rotation dispersion remains the same in all the solutions. This was shown by Gennari[1] with mixtures of nicotine with water, methyl alcohol, ethyl alcohol and benzene.

Finally, as regards the effect of temperature on rotation dispersion, Gernez[2] has observed that the dispersion suffers no change in turpentine oil, orange oil, bitter orange oil and camphor, and not even when, by aid of heat, the substances are brought into the condition of vapor.

46. **Anomalous Rotation Dispersion.**—With certain substances in solution the phenomenon is observed that the rotation of the plane of polarization does not change regularly with increasing refrangibility (or decreasing wave-length) of the rays, but that for some color lying between the red and violet ends of the spectrum it has a maximum, or, also, a minimum. Further than this, the rotation may be the same for a number of different rays Such anomalies, which, as is known, may appear also in respect to refractive dispersion have been observed in the following substances

d-Tartaric Acid.—The irregularities in the rotation dispersion of this substance were discovered by Biot[3] and later investigated by Arndtsen[4] The latter determined the increase in the specific rotation of the acid in solutions of decreasing percentage strength, for different Fraunhofer lines, employing the method of Broch, and calculated the following interpolation formulas, holding for a temperature of 24°, q representing the percentage amount of water present:

Spectral lines	Wave-length. μμ	
C	656.2	$[\alpha] = +2.748 + 0.0945\,q$
D	589.2	$[\alpha] = +1.950 + 0.1303\,q$
E	526.9	$[\alpha] = +0.153 + 0.1751\,q$
b_1	518.3	$[\alpha] = -0.832 + 0.1915\,q$
F	486.1	$[\alpha] = -3.598 + 0.2398\,q$
e	438.3	$[\alpha] = -9.657 + 0.3144\,q$

If from these formulas, which hold to $q = 40$ (the strongest solution of tartaric acid which can be made at 24° contains 60 per cent of the acid), but which certainly apply for $q = 30$, we calculate the specific rotations of solutions containing from 30 to 90 per cent of water, we obtain the following numbers, given in order of increasing concentration·

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[1] Gennari: Ztschr. phys. Chem., 19, 130 (1896).

[2] Gernez: Ann. de l'ecole norm., 1, 1.

[3] Biot. Mem. de l'Acad., 15, 93 (1838).

[4] Arndtsen: Ann. chim. phys., (3), 54, 403. Pogg Ann., 105, 312.

In 100 parts of solution		Red	Yellow	Green.	Green	Greenish blue	Blue
Water q	Tartaric acid	$[\alpha]_C$	$[\alpha]_D$	$[\alpha]_E$	$\alpha]_b$	$[\alpha]_F$	$[\alpha]_e$
90	10	11 25°	13 68°	15 92°	16 40°	17.98°	18.64°
80	20	10 30	12 37	14 16	14.49	15 59*	15.49
70	30	9 36	11 07	12.41	12 57	13.19*	12 35
60	40	8 42	9 77	10 66	10 66	10.79*	9.21
50	50	7 47	8 47	8 91*	8 74	8 39	6.06
40	60	6.53	7 16*	7 16*	6 83	5 99	2 92
30	70	5 58	5 86*	5 41	4 91	3.60	—0 23

From this table it is evident that for some particular color each solution shows a maximum in its rotating power which is indicated by a * For the weakest solution, with ten per cent of tartaric acid, the maximum occurs normally at the color of greatest refrangibility, *e*, but with increase of concentration it passes gradually toward the red end of the spectrum, the 50 per cent solution exhibiting the maximum rotation for the green ray, and the 70 per cent. solution for the yellow. In these cases the rotation, after passing the maximum point, decreases with increase in refrangibility and becomes finally negative for blue light with the most concentrated solution. This solution must therefore be perfectly inactive for some color between *F* and *e*. It is also evident that for certain concentrations different rays are rotated through the same number of degrees; thus the specific rotation of the solution with 40 per cent. of acid is 10.66° for *E* as well as for *b*, and for the 60 per cent. solution it is the same for *D* and *E*, *viz.*, 7.16°.

The left-hand rotation which with a 70 per cent. solution appears for blue light, would increase and show even with the less refrangible rays, if it were possible to pass to more concentrated solutions. The anhydrous acid, whose specific rotation is expressed by the first constants of the Arndtsen formulas, must, as shown by the sign, exhibit right-hand rotation for the rays *C*, *D* and *E*, and left-hand rotation for *b*, *F* and *e*. In fact, Biot[1] was able to observe such opposite rotation with plates made by pouring a mixture of tartaric acid melted with a little water; and Arndtsen[2] found that left rotation for the strongly refrangible rays is shown when concentrated alcoholic solutions of the acid are used.

The anomalies in the rotation dispersion of tartaric acid disappear when the solutions are examined at a higher temperature (Krecke),[3] or when a little boric acid is added (Biot). They are not shown with the salts of tartaric acid (Biot), which fact has recently been confirmed by Rimbach[4] in the case of rubidium tartrate.

Malic Acid.—The rotating power for different kinds of light has been investigated by B. A. Woringer[5] by aid of the ray-filter method, and using solutions, the amount of water in which, q, varied from 49 per cent. to 93 per cent. The following interpolation formulas were derived, based on a temperature of 20°

Red .... $\lambda = 665.9\ \mu\mu$, $[\alpha] = 4.605 - 0.0709\,q$
Yellow .... " $= 591.9$ " " $= 6.544 - 0.0957$ "
Green .... " $= 533.0$ " " $= 8.349 - 0.1128$ "
Light blue....... " $= 488.5$ " " $= 10.121 - 0.1298$ "
Dark blue .... " $= 448.2$ " " $= 14.971 - 0.1730$ "

The specific rotations calculated from these are

TABLE I

Malic acid	Water.	Red	Yellow	Green	Light-blue	Dark-blue
p	q					
50	50	+ 1.06	+ 1.76	+ 2.71	+ 3.63	+ 6.33
40	60	+ 0.35	+ 0.81	+ 1.58	+ 2.33	+ 4.59
30	70	-- 0.56	+ 0.15	+ 0.45	+ 1.03	+ 2.86
20	80	— 1.07	— 1.11*	— 0.67	— 0.27	+ 1.13
10	90	— 1.78	— 2.07*	— 1.80	— 1.56	— 0.59
8	92	— 1.92	— 2.26*	— 2.03	— 1.84	— 0.95
5	95	— 2.13	— 2.55*	— 2.37	— 2.23	— 1.47

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[1] Biot. Ann. chim. phys., [3], **28**, 351

[2] Arndtsen. Ann. chim. phys., [3], **54**, 415

[3] Krecke. Arch. Neérland., **7**, (1872).

[4] Rimbach: Ztschr. phys. Chem., **16**, 671

[5] Woringer. Investigations in the author's laboratory, not yet published (1898).

In another series of observations carried out by Nasini and Gennari,[1] in which the ray-filter method was employed, the yellow light, however, being that of the sodium flame, the following specific rotations, for a temperature of 20° were obtained:

TABLE II.

No	d_4^{20}	p	q	$[\alpha]_{red}$	$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{lb}$	$[\alpha]_{db}$
1	1.3454	72 79	27.21	+ 1 80°	+ 2.86°	+ 3.90°	+ 5.20°	+ 6 39°
2	1.2723	59 02	40 98	+ 1 35	+ 2.08	+ 3.05	+ 4.21	+ 5 63
3	1.1861	42.80	57.20	+ 0.19	+ 0.55	+ 1.18	+ 2 08	+ 3.29
4	1 1423	34 27	65 73	— 0.18	+ 0.07	+ 0.51	+ 1.64	+ 2.20
5	1.1395	33.24	66 76	— 0.41	— 0.31	+ 0 07	+ 0.46	+ 0.86
6	1 1239	30.02	69 98	— 0.51	— 0 42	— 0.05	+ 0.29	+ 0.72
7	1 1193	28 72	71.28	— 0.79	— 0 67	— 0 46	— 0.22	+ 0.29
8	1.1034	25 67	74 33	— 0.94	— 0 81	— 0.69	— 0 39	+ 0 14
9	1 0663	16.84	83 16	— 1 07	— 1.28*	— 1.05	— 0 62	0 00
10	1.0635	16 24	83 76	— 1 28	— 1 46*	— 1.30	— 0 91	— 0 36
11	1 0304	8 23	91.77	— 1 09	— 1 09	— 1.08	— 1.09	— 1 08
12	1 0156	4.61	95.39	— 1.87	— 1 17	— 2 56	— 2.45	— 2.51

From these two tables the following appears

1. Concentrated solutions of malic acid, with amounts of water varying from 27 to 60 per cent, exhibit right hand rotation for all colors, which increases normally with the refrangibility of the rays.
2. In solutions with $q = 66$ to 75 per cent. (4 to 8 in Table II) the less refrangible rays rotate to the left and the stronger to the right. The point of inactivity which is passed here moves, with increasing dilution, toward the violet end of the spectrum.
3. Anomalous dispersion is shown in solutions containing more than 80 per cent. (Table I) or 83 to 84 per cent. of water (Table II, No 9 and 10); a maximum rotation (+) is shown for yellow rays
4. In Table II the phenomenon appears that in a solution with about 92 per cent of water there is equally strong rotation for all colors, and that one with $q = 95$ shows a minimum rotation for yellow light, and then increasing left-hand rotation toward the violet end.

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[1] Nasini and Gennari: Ztschr. phys. Chem., 19, 113 (1891)

There is less certainty about these observations however, because in such weak solutions the observed angles of rotation are very small Such anomalies do not appear in the results calculated for $q = 92$ and 95 from the interpolation formulas of Woringer, but a maximum is shown for the yellow rays.

Boric acid does not correct the irregularities in the dispersion of malic acid (Nasini and Gennari).

Equimolecular Mixture of Nicotine and Glacial Acetic Acid, Treated with Water.—In such combinations, Gennari[1] has observed the appearance of anomalous dispersion, but only within very narrow limits of concentration. The specific rotation of nicotine was found in the following mixtures by means of the ray-filter method (for yellow, the sodium flame however) at a temperature of 20° .

		$[\alpha]_{red}$	$[\alpha]_{D}$	$[\alpha]_{gr}$	$[\alpha]_{lb}$	$[\alpha]_{db}$
Pure nicotine $d_4^{20} = 1\ 0107$		—123.37	—162 84	—209 78	—250 71	—317 79
Equimolecular mixture of nicotine and glacial acetic acid		—55 63	— 74 18	— 95 22	—120 3	—143.54
Mixtures of the same with water						
Original mixture	Water q					
81 26	18 74	—9 20	—12 57	—16 83	—21 99	—26 68
78 87	21 13	—4 13	—5 82	—8 20	—10.92	...
77 84	22 16	—1 70	—2 73	—4 39	—6 63	—9.93
77 45	22 55	—0 12	—0 54	—1 48	—2 80	—5 00
76 39	23 61	+0 78	+0.52	...	—0 75	..
76.30	23.70	+1.36	+0 98	+0 74	....	—1 40
76 23	23.77	+5 90	+7 44	+8 85	+9 87	. .
76.10	23 90	+12 92	+16.74	+20 72	+24 56	+28 00
Specific rotation of nicotine acetate						
Salt.	Water					
53.72	46.28	+16.44	+21 36	+25.81	+29 05	.
44 30	55.70 *	+14.30	+18.85	+22 83	+26.57	+31 37
26 48	73 52	+13 21	+17 35	+21 23	+23 98	. ..
24.28	75 72	+1[illegible] 00	+16 96	+20 41	+23.50	+25.84

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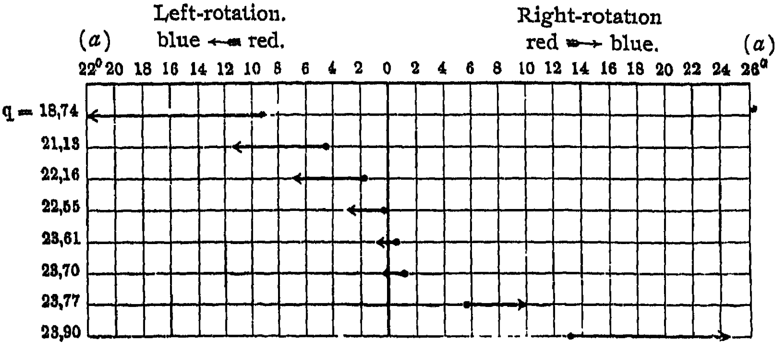
[1] Gennari: Ztschr phys Chem, 19, 130.

As immediately apparent, pure nicotine and the mixture of this with one molecule of acetic acid possesses a normal left-hand rotation, increasing with the refrangibility of the light. As nicotine acetate rotates to the right it appears that a part of the nicotine in the mixture must exist in the uncombined condition.

The peculiarities in dispersion which appear when water is added to the equimolecular mixture of acetic acid and nicotine, can be best seen from the following diagram. This extends from the red only to light blue, as [α] for dark blue had to be omitted on account of incompleteness in the observations:



It will be seen that

1. In mixtures with 18 74 to 22.55 per cent. of water there is normal left-hand rotation for the different colors and that this decreases, the dispersion also, with increasing amount of water.

2. The solutions containing from 23.77 to 23.90 per cent. of water possess right rotating power, which, with the dispersion, increases in marked degree by the slight increase in the amount of water.

3. With an amount of water varying from 23.61 to 23.70 per cent., the rotation and also the dispersion are very small, the first solution showing complete inactivity for green rays and the second for light blue rays. We have here then the case of appearance of a minimum of rotation with increasing refrangibility of the light.

Nicotine acetate shows normal dispersion in solutions containing 46 to 76 per cent. of water, as appears from the above table.

Of interest finally are the conditions of dispersion in solutions of *nicotine in acetone*, *ethyl alcohol* and *propyl alcohol*, for which Nasini and Gennari[1] found the following specific rotations:

	p	c	$[\alpha]_{red}$	$[\alpha]_D$	$[\alpha]_{gr}$	$[\alpha]_{lb}$	$[\alpha]_{db}$
Acetone	22.00	20.77	— 4.93	— 6.01	— 7.10	— 7.53	— 8.90
Ethyl alcohol. .	21.40	19.09	— 5.73	— 7.09	— 9.01	— 9.71	— 10.32
Propyl alcohol..	21.15	19.06	— 3.30	— 3.62	— 3.92*	— 3.88	— 3.07

The rotation and dispersion of nicotine in these solutions are seen to be very much decreased With the propyl alcohol there is even anomalous dispersion as the green ray appears to have suffered the greatest deviation

In regard to the explanation of anomalous rotation dispersion, Biot[2] has shown at length that the phenomenon must appear when the ray of light passes two liquid layers which rotate the plane of polarization in opposite directions, and which at the same time possess different dispersive powers He employed in experiments left-rotating turpentine and a solution of right-rotating camphor in acetic acid, which were contained in tubes placed one behind the other, and showed by calculation how the length of the column of the camphor solution and its concentration must be changed to reach a maximum or minimum of rotation for a given ray. That a perfect achromatism, that is equally strong rotation for all rays is possible, has been shown by investigations of Nasini and Gennari.[3]

The same conditions naturally obtain when two oppositely rotating liquids are mixed in different proportions. Thus, v. Wyss[4] was able to show a maximum of rotation for yellow light of wave-length 565 $\mu\mu$ in mixtures of right and left turpentine oil. Further, Gennari[5] found that if to a solution of right-rotating nicotine sulphate, left-rotating nicotine be added gradually, in small portions, the rotation for the different colors grows less and less, and that finally the left rotation of the nicotine appears in increasing degree for all rays. There is here the same condition as with the above-mentioned mixtures of nicotine, acetic acid and water, and the phenomena which these exhibit may be explained by assuming that the different solutions contain at the same time right-rotating nicotine acetate and left-rotating free nicotine in variable proportions.

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[1] Nasini and Gennari. Ztschr. phys chem , 19, 117

[2] Biot Ann. chim phys , [3], 36, 405 (1852)

[3] Nasini and Gennari *loc. cit*, p 121

[4] v Wyss Wied Ann., 33, 554 (1888)

[5] Ztschr phys Chem , 19, 134 (1896)

But on what the anomalous dispersion of the aqueous solutions of malic acid and tartaric acid depends, has not yet been definitely shown. An attempt at an explanation will be referred to later in §63.

Finally, a special class of anomalous dispersion phenomena must be mentioned, which appear when the active solutions are colored. If white light is sent through these, absorption of some of the rays follows, and the rotation of those remaining does not then change regularly with the wave-lengths Cotton[1] has investigated such conditions in solutions of copper tartrate and chromium tartrate in potash.

[1] Cotton Compt rend, **120**, 989, 1044, Ann chim phys, [7], **8**, 347 (1896)

PART THIRD

Numerical Values for the Rotating Power. Specific Rotation

47. In the measurement of the optical activity of liquids and dissolved bodies, Biot[1] introduced in 1835 the conception of *specific rotation*, indicating by this term, *the angle of rotation* $[\alpha]$, *which a liquid would show if it contained in a volume of 1 cubic centimeter, 1 gram of active substance, and should act on the polarized ray through a column 1 decimeter in length*

As already explained in the introduction, §2, the specific rotation of bodies, in themselves liquids, is expressed by the formula

$$[\alpha] = \frac{\alpha}{l \cdot d} \tag{I}$$

in which

α = the angle of rotation measured for a ray of definite wave-length,
l = the length of the observation tube in decimeters,
d = the specific gravity of the liquid, referred to water at 4° as standard.

In the measurement of these three quantities, the temperature must always be considered, and should be kept the same for all As normal temperature, 20° C. is usually taken.

The specific rotation of an active liquid for a given light and temperature, for example, $[\alpha]^{20}_{D}$, *expresses a characteristic constant for this substance.*

For solid active substances which are brought into solution by aid of an inactive solvent, the specific rotation may be derived in two ways, on the assumption that α is proportional to the concentration :

1. With determination of the concentration, c, by which is

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[1] Biot Mém de l'Acad, 13, 116 (1835) Ann chim. phys, [3], 10, 5.

understood the number of grams of active substance dissolved to make 100 cc. of solution, we have the formula:

$$\text{(II)} \qquad [\alpha] = \frac{\alpha \, . \, 100}{l \, . \, c};$$

2. With the determination of the percentage strength, p, of the solution, by which is understood the number of grams of active substance in 100 grams of the solution, and further of the specific gravity, d, of the solution. We have then the formula:

$$\text{(III)} \qquad [\alpha] = \frac{\alpha \, . \, 100}{l \, . \, p \, . \, d}$$

in which $p d = c$.

In many cases, especially where we are concerned with single values for the specific rotation, the experimentally simpler determination by formula (II) is sufficient. A solution is made in a flask holding 100 true cc. at 20°, and this is polarized at the same temperature. But if it is desired to follow changes in the specific rotation corresponding to changes in the composition of the solution, it is necessary to prepare the latter by weighing the active substance and the solvent, as the percentage amounts of both must be known. It then remains to find the specific gravity of the solution at 20° referred to water at 4°, determine the angle α, and calculate according to formula (III).

The details of practical methods are given in Part IV.

As experience has shown the specific rotation calculated from solutions is seldom a constant number; with most substances the value changes through several influences in a more or less marked degree, being dependent on:

1. The concentration of the solution.
2. The nature of the solvent.
3. The temperature.

A detailed discussion of these relations will be given in the following chapters.

I. CONSTANT SPECIFIC ROTATION OF DISSOLVED SUBSTANCES

48. **Cane-Sugar** was the first substance whose specific rotation was determined by Biot in 1835 and he found that for a con-

stant length of the observation tube the angle of rotation was proportional to the amount of sugar in solution; in other words, the same value resulted for $[\alpha]$ whatever concentration of the solution was employed. The same was found for mixtures of turpentine and ether. Biot, assuming from such results, that the amount of rotation is simply proportional to the number of active molecules passed by the light in going through the solution, reached the following law:

> "When an active substance is dissolved in an inactive solvent, which produces no chemical change, the angle of rotation observed is proportional to the amount by weight of the active substance in the unit volume of solution, and the specific rotation is therefore a constant quantity."

According to our present knowledge, however, perfect constancy in the values for $[\alpha]$ are shown by but few substances. Even with cane-sugar later more exact investigations have shown that with decreasing concentration of the aqueous solution the specific rotation increases slightly, it being in fact found that by changing the percentage strength from 65 to 2 per cent of sugar, the value $[\alpha]_D$ increases uniformly from 65.62° to 66 80°, that is about 1 8 per cent (See § 52.) On the other hand in certain cases even with great variations in the concentration no such regular change in the rotation could be found, for example

Milk-Sugar which was investigated in 32 aqueous solutions varying in strength from $p = 2.35$ to $p = 36$ per cent., gave for the specific rotation numbers which varied irregularly between the limits $[\alpha]_D^{20} = 51\ 94^\circ$ and 53.18°. The mean of all determinations was $[\alpha]_D^{20} = +52.53^\circ$ for $C_{12}H_{22}O_{11}.H_2O$ (Schmöger).[1]

Rhamnose shows between the limits $c = 3$ to 30 the constant specific rotation $[\alpha]_D^{20} = +8.50^\circ$ for $C_6H_{12}O_5.H_2O$ (Schnelle and Tollens).[2]

Parasantonide in Chloroform.—Of this very strongly rotating substance 13 solutions, varying in strength from $p = 0.14$ to 48 per cent., gave rotations between $[\alpha]_D^{20} = +887.9^\circ$ and

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[1] Schmoger Ber d chem. Ges., 13, 1922

[2] Schnelle and Tollens Ann Chem. (Liebig), 271, 64.

896.5°. The mean of all observations was $[\alpha]_D^{20} = + 890.9°$ which differs from the extreme values by only 0.5 per cent. The rotation is constant for other light rays than *D*. The temperature likewise did not seem to exert any appreciable influence. In solutions of the body in alcohol, however, for the slight change in concentration from $p = 0.26$ to $p = 8.5$ a change from $[\alpha]_D^{20} = + 880$ to $[\alpha]_D^{20} = + 833.9$ followed (Nasini)[1]

Santonide, dissolved in chloroform, for all concentrations between $c = 3$ and 30 and for all kinds of light shows a constant specific rotation For example, for yellow, $[\alpha]_D = + 754$ (Nasini).[2]

Nicotine, which possesses the specific rotation $[\alpha]_D^{20} = - 164°$ dissolved in benzene gave the following numbers.

Nicotine.	$[\alpha]_D^{20}$	Nicotine	$[\alpha]_D^{20}$
$p = 84.36$	$-164.29°$	$p = 19.00$	$-163.95°$
48.02	-164.14	16.36	-163.88
25.47	-164.10	8.52	-163.67

Mean $[\alpha]_D^{20} = - 164.00°$

There is therefore here but a very small change in the specific rotation, amounting to only 0.2 per cent (Hein)[3]

In like manner the specific rotation of nicotine remains almost unchanged when it is dissolved in ether or acetone, while with aniline and toluidine there is a slight decrease, to about $[\alpha]_D^{20} = - 156.5$ (Hein). The decrease in ethyl or propyl alcohol is somewhat more, while with water it is very marked. (See § 52.)

Cocaine, dissolved in chloroform, shows for solutions varying from $p = 10$ to 25, specific rotations which are always between $[\alpha]_D^{20} = - 16.28°$ and $- 16.36°$ (Antrick)[4]

With several other substances, for example, *d-camphor* dissolved in almond oil or olive oil (Aignan),[5] and *l-α-camphol* dissolved in alcohols, acetone, acetic ether or hydrocarbons (Haller)[6] constancy in the specific rotation was found, but the experiments covered but small variations in concentration.

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[1] Nasini Ber d chem Ges, 14, 1512

[2] Nasini Accad d Lincei, [3], 13 (1882)

[3] Hein Inaug Diss, Berlin (1896)

[4] Antrick Ber d chem Ges., 20, 321

[5] Aignan See next paragraph.

[6] Haller Compt rend, 112, 143

As is apparent, therefore, the Biot law given above possesses but a limited applicability.

II. VARIABLE SPECIFIC ROTATION OF DISSOLVED SUBSTANCES

A. Dependence of the Specific Rotation on the Concentration of the Solutions

49. In the investigation of aqueous solutions of tartaric acid, Biot[1] found in 1838, that the specific rotation of this substance was the larger, the more dilute the solution employed. This case was considered a long time as an exception, until in 1852, with the aid of better polarization apparatus, Biot[2] recognized that the phenomenon appears with other substances also. Thus, with increasing dilution of its solutions in alcohol or acetic acid camphor showed a decrease in specific rotation, turpentine on the contrary, by increasing additions of alcohol or olive oil an increase, and finally, even with sugar, a slight increase was observed with an increase in the amount of water. Besides this, the influence of the solvent was brought to light, as in the case of camphor different values for [α] were obtained by dissolving it in alcohol or in the same amount of acetic acid. Biot then noted clearly the fact, that in general the values of specific rotations calculated from solutions are more or less variable numbers, and that consequently the molecules of the active substances seem to suffer some alteration by the presence of the inactive solvent particles.[3]

For a long time, however, this widening of our knowledge of specific rotation remained largely unnoticed. The fact that in solutions of cane-sugar, the angle of rotation is almost exactly proportional to the concentration, and that accordingly from the observed angle of rotation, the amount of sugar can be calculated, led to the construction of the optical saccharimeters which soon became extensively used, and were also employed in the investigation of other substances. In spite of the fact that Biot[1] in 1860 had published an extended paper, which contained a résumé of all his work in this field, and again called attention to the correct relations, the opinion was still in the main held that active substances in general behave as does cane-sugar; it was therefore considered sufficient in the optical examination of a substance to determine the rotation for a single solution and then, from this, by aid of formula II or III, to calculate the specific rotation and consider this as constant. In this way, a great many specific rotations have been determined, which, generally with no mention of the concentration or solvent employed, have slipped into the physical and chemical handbooks and have been retained for a long time.

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[1] Biot. Mém. de l'Acad., 15, 93; Ann. chim. phys., [3], 10, 385.

[2] Biot. Ann. chim. phys., [3], 36, 257.

[3] Several French investigators as Aignan (Pouvoir rotat. spec. d. corps act. dissous. Thèse, Paris, 1893, and Freundler, (Ann. chim. phys., [7], 4, 244, (1895)) refer to the constancy of [α] as Biot's law and state the case as if I (Landolt: Ann. Chem. (Liebig), 189, (1877)) had first shown its inaccuracy, whereas, this had long since been shown by Biot himself.

In 1873 Oudemans[2] independently found that the specific rotation can assume very different values when different inactive liquids are used as solvents. Hesse[3] published in 1875 a large number of determinations of rotations, of over fifty active substances, and in solutions of different concentrations. Even with only small variations in the latter (between 1 and 10 grams in 100 cc) nearly all bodies exhibit marked differences in specific rotation, and in most cases a decrease in this with increase in concentration Still greater differences, amounting often to over 50 per cent , were found by varying the liquids employed as solvents The numerous investigations which have been carried out in the last twenty years on the rotation of new organic substances have led to the same results

50. The Determination of the True Specific Rotation of Dissolved Substances, According to Biot.—Only such value can be given to the specific rotations calculated from a single solution as attaches to a constant obtained under special conditions. But Biot[4] showed long ago in his investigations on the rotation of tartaric acid how a definite meaning may be given to these variable numbers and this is explained in the following considerations:

[1] Biot: Ann. chim phys, [3], 59, 206

[2] Oudemans: Pogg. Ann, 148, 337: Ann Chem (Liebig), 166, 65

[3] Hesse Ann. Chem. (Liebig), 176, 89, 189.

[4] Biot· Mém. de l'Acad, 15, 205 (1838); 16, 254 (1838), Ann chim. phys [3], 10, 385 (1844), 28, 215 (1850); 36, 257 (1852); 59, 219 (1860)

For liquid active substances the specific rotation may be directly determined, and for a given temperature this is a constant. If now such a body, for example turpentine, be mixed in different proportions with an indifferent liquid, such as alcohol, and then from the percentage amount, the specific gravity and observed rotation, the specific rotations be calculated, values result which differ more or less widely from that found for the pure substance. The original rotation of the body undergoes then a change by reason of the presence of the inactive molecules, most active substances showing an increase in rotation; a few, however, a decrease in specific rotation by increase in the amount of the solvent.[1]

If the active body is solid it can be investigated only in solution, and, according to the constitution of the latter, different numbers for the specific rotation are obtained which do not represent the real specific rotation of the pure substance but values modified by the presence of the inactive solvent and differing from the first to an extent which is quite unknown.

If a pure homogeneous liquid is employed as solvent so that indifferent molecules of one and the same kind only affect the molecules of the active body, changes in the specific rotation may be followed most readily by graphic representation by taking the percentage amounts of inactive solvent (q) as abscissas in a coordinate system, while the corresponding values for $[\alpha]$ are taken as ordinates An increase or decrease in the specific rotation is often shown then as a straight line which inclines in proportion to changes in q and which may be represented by the general formula

$$\text{(I)} \qquad [\alpha] = \mathrm{A} + \mathrm{B}\,q,$$

the constants in which, A and B, may be calculated from the experiments. In other cases, on the contrary, the line obtained is not straight, but is a curve, ordinarily a part of a parabola or hyperbola, in which case the dependence of the specific rotation on q is shown by an expression of the form

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[1] This could be seen by aid of a polarization apparatus placed vertically, the observation tube being left open above. Let turpentine oil, for example, be poured into the tube and say 1 cm in height, and the rotation then observed Now by adding increased amounts of alcohol, and observing, greater and greater rotations will be found The number of active molecules is the same throughout, but they are distributed through a lengthened column By employing nicotine and diluting gradually with water a constantly decreasing rotation would be found.

$$\text{(II)} \qquad [\alpha] = A + Bq + Cq^2 \text{ or } [\alpha] = A + \frac{Bq}{C+q},[1]$$

or by some other equation with several constants.

In these formulas, A represents the specific rotation of the pure substance, and the values for B, formula (I), and for B and C, formula (II), represent the increase or decrease which A suffers by the presence of 1 per cent. of inactive solvent.

If $q = 0$ we have the specific rotation of the pure substance; if, on the other hand, in equations I and II we put $q = 100$, there results for $[\alpha]$ a value which must be looked upon as the specific rotation of the body in solution of infinite dilution. If we assume that in the case $q = 100$, the active body has entirely disappeared, and the liquid consists of the inactive solvent only, the rotation then must become 0 This, according to Biot,[2] may also be derived from the above expressions by putting them equal to the equation $[\alpha] = \frac{\alpha \, . \, 100}{l \, p \, . \, d}$, which represents the specific rotation as calculated directly from th observed rotation α. If in the last equation, in place of p

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[1] The three constants, A, B and C of the formula $[\alpha] = A + \frac{Bq}{C+q}$ may be found according to Biot (Ann chim phys, [3], 11, 96, § 69) in the following way, if for thre solutions with q_1, q_2 and q_3 per cent of inactive solvent, the corresponding specifi rotations, $[\alpha]_1$, $[\alpha]_2$ and $[\alpha]_3$ have been determined

If we take

$$A + B = a, \qquad BC = b, \qquad C = c,$$

then the values for a and c follow from these equations.

$$([\alpha]_2 q_2 - [\alpha]_1 q_1) + ([\alpha]_2 - [\alpha]_1) c - (q_2 - q_1) a = 0,$$
$$([\alpha]_3 q_3 - [\alpha]_1 q_1) + ([\alpha]_3 - [\alpha]_1) c - (q_3 - q_1) a = 0,$$

and therefore b from each of the following equations.

$$([\alpha]_1 - a)\ (q_1 + c) = -b,$$
$$([\alpha]_2 - a)\ (q_2 + c) = -b,$$
$$([\alpha]_3 - a)\ (q_3 + c) = -b,$$

Finally we have

$$a - \frac{b}{c} = A, \qquad \frac{b}{c} = B, \qquad c = C$$

Biot brings the equation

$$[\alpha] = A + \frac{Bq}{C+q}$$

also into the form:

$$[\alpha] = A + \frac{B'q}{1 + C'q} \quad \text{in which} \quad B' = \frac{B}{C} \quad \text{and} \quad C' = \frac{1}{C}$$

Instead of q in the above formulas we can naturally introduce p and write

$$[\alpha] = A + B\,(100 - p),$$
$$[\alpha] = A + B\,(100 - p) + C\,(100 - p)^2.$$

[2] Biot: Ann. chim. phys., [3], 10, 399, § 59; 59, 224, § 15.

inasmuch as $p + q = 100$, we put the value $100 - q$, and take, for example, using formula (I),

$$\frac{\alpha \; 100}{l.d\,(100 - q)} = A + Bq,$$

there follows

$$\alpha = l.d \left[A + \left(B - \frac{A}{100} \right) q - \frac{B}{100} q^2 \right].$$

If in this equation we place $q = 100$, then $\alpha = 0$; that is, the rotation has disappeared. If, on the other hand, $q = 0$ then there results $\alpha = l.d.A$, that is the angle of rotation which a column of the pure active substance l dm long with the specific gravity d shows From this $\frac{\alpha}{ld} = A$ results and as at the same time $\frac{\alpha}{ld} = [\alpha]$ it follows that $[\alpha] = A$, that is, the specific rotation of the pure substance without solvent.

With active liquid bodies which may be mixed in all proportions with the inactive solvent, the change in the original specific rotation may be followed by experiment to the most dilute solutions, and consequently the whole curve from $q = 0$ to nearly $q = 100$ may be constructed If from a number of solutions in this case the constant A be calculated, a value must result which agrees the more perfectly with the real specific rotation of the pure substance, the larger the portion of the curve covered by the observations and the nearer this approaches the abscissa $q = 0$, that is the greater the corresponding concentration

If the active substance is solid its original specific rotation can not be directly determined, and at the same time, depending on the conditions of solubility, only a more or less complete portion of the curve may be established, beginning at some distance from the zero-point of the coordinate system. If the constants of the formulas (I) and (II) be calculated from the observations made, the values obtained can be used for interpolation with accuracy only within the limits of concentration embraced by the solutions used for the experiments.

It may be asked now, how far one is justified in such a case in looking upon the value obtained for A as representing the specific rotation of the pure substance. The extrapolation which is made here is allowable when the change in the specific rotation is represented by a straight line, that is by the formula $[\alpha] = A + Bq$ If, however, it is a curve, the A calculated from the formula $[\alpha] = A + Bq + Cq^2$ (or some other one) will represent the true specific rotation, the less accurately, the smaller the portion of the curve which could be obtained. How far this end may be reached depends, therefore, on the greater or less solubility of the active body. I only dilute solutions of it may be prepared, and if it appear at the same time that the values for $[\alpha]$ do not increase o decrease linearly with q, then there is no hope that the specifi rotation of the pure substance may be reached.

If in formulas (I) and (II) instead of q, the amount o active substance in 100 parts of solution, that is, p, be taken then the constant A represents the specific rotation in condition of infinite dilution, and the rotation of the pure substance follows when $p = 100$ is taken. But the use of q is t be preferred, according to the above explanations.

In finding the specific rotation according to the formul $[\alpha] = \frac{\alpha . 100}{l . c}$ the determination of the specific gravity of th solution is omitted, and only the concentration, c, by aid of flask of known volume, determined. If we change then th above equations (I) and (II) into $[\alpha] = \mathfrak{A} + \mathfrak{B}c$ and $\mathfrak{A} + \mathfrak{B}c -$ $\mathfrak{C}c^2$ and place $c = 100$, there results the specific rotation for solution which contains in 100 cc. 100 grams of active substanc But this would represent the pure substance only when i specific gravity is equal to unity; but if this is different, = which is practically always the case, then for the value c, 100 must be substituted This requirement can be satisfied b rarely, and even then not with certainty, as it assumes knowledge of the specific gravity of the active substance in unknown amorphous condition; numerical values, therefo of specific rotations coupled only with the concentratic without definite statements as to the specific gravity a percentage composition of the solutions, can not be used calculate the true specific rotation of the substance free fr solvent.

Finally, with reference to crystallized bodies, it must be understood that the constant A, calculated from their solutions, expresses, as a matter of course, only the rotation which is characteristic of the molecule. This value may be very different from the specific rotation which belongs to the solid crystal, as shown in § 7, because here, besides the molecular rotation, the crystal rotation comes into play also

51. **Reduction Formulas.**—Alterations in specific rotation of dissolved bodies may be expressed, as explained above, as functions of

1. The percentage amount of inactive solvent, q:

$$\text{(I)} \qquad [\alpha] = A + Bq + Cq^2;$$

2. The percentage amount of active substance, p:

$$\text{(II)} \qquad [\alpha] = a + bp + cp^2;$$

3. The concentration, c, or grams of active substance in 100 cc. of solution.

$$\text{(III)} \qquad [\alpha] = \mathfrak{A} + \mathfrak{B}c + \mathfrak{C}c^2,$$

in which case, however, the constant, $\mathfrak{A}$, has no definite meaning.

In many cases the third constant in these expressions disappears.

For transformation of the constants of the equations (I) and (II) we take:[1]

$$\begin{array}{l|l} a = A + 100\,B + 10{,}000\,C & A = a + 100\,b + 10{,}000\,c \\ b = -B - 200\,C & B = -b - 200\,c \\ c = C & C = c \end{array}$$

Thus Tollens[2] established the following formula for cane-sugar in an aqueous solution which holds within the limits, $p = 3$ to $p = 69$ per cent.,

$$[\alpha]_D = 66.386 + 0.015035p - 0.0003986\,p^2,$$

from which follows for $q = 31$ to 97 per cent ,

$$[\alpha]_D = 63.904 + 0.064686\,q - 0.0003986\,q^2.$$

---

[1] The calculation of A from equation (II) follows by taking in equation (I) $q = 0$ and in (II) $p = 100$ and then equating the two On the other hand a follows from equation (I) when in (I) we take $q = 100$ and in (II) $p = 0$

As $p + q = 100$ we have further the equations

$$A + B\,(100 - p) + C\,(100 - p)^2 = A + 100\,B + 10{,}000\,C + bp + cp^2,$$
$$a + b\,(100 - q) + c\,(100 - q)^2 = a + 100\,b + 10{,}000\,c + Bq + Cq^2,$$

from which the relations between B and b, and C and c follow

[2] Tollens Ber d chem Ges, **10**, 1410 , **17**, 1757.

Landolt[1] found for camphor dissolved in benzene within th limits $q = 37$ to $q = 76$:

$$[\alpha]_D = 55.21 - 0.1630q,$$

from which follows for $p = 24$ to 63 per cent.,

$$[\alpha]_D = 38.91 + 0\ 1630p.$$

It is sometimes required to change the constants of th equation

$$[\alpha] = a + bp + cp^2,$$

for a substance with molecular weight M so that they wil apply for a derivative (hydrate, salt, etc.) with the molecula weight M_1. Then the above formula becomes .

$$[\alpha] = a_1 + b_1p + c_1p^2,$$

and the constants of this are found ·[2]

1. In the case, $M < M_1$ from

$$a_1 = a\frac{M}{M_1}, \qquad b_1 = b\left(\frac{M}{M_1}\right)^2 \qquad c_1 = c\left(\frac{M}{M_1}\right)^3.$$

2. In the case, $M > M_1$ from

$$a = a\frac{M_1}{M}, \qquad b_1 = b\left(\frac{M_1}{M}\right)^2, \qquad c_1 = c\left(\frac{M_1}{M}\right)^3$$

For example, the following equation was established b Tollens[3] for anhydrous glucose, $C_6H_{12}O_6$, $M = 180$·

$$[\alpha]_D = 52.50 + 0.018796p + 0.00051683p^2$$

From this there may be derived for the hydrate, $C_6H_{12}O_6$ - H_2O, $M_1 = 198$, the following formula, taking into considera tion that $M < M_1$

$$[\alpha]_D = 47.73 + 0.015534p + 0\ 00038830p^2.$$

52. Experimental Proof of Biot's Formulas.—With what degre of certainty the true specific rotation of a substance may l calculated from observations on its solutions can be determine by experiments on active liquid bodies. First, the specif rotation is found directly, and then a number of mixtures wit inactive liquids are prepared and from the observed rotatio in these the constants in the formula $[\alpha] = A + Bq$ or $[\alpha] =$

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[1] Landolt: Ann Chem (Liebig), 189, 334.

[2] In the introduction, §2, the calculation is carried out only for the case $M < M_1$.

[3] Tollens Ber. d. chem Ges, 17, 2238.

$A + Bq + Cq^2$ are derived. The values obtained for A by using different solvents must all agree very closely with the observed value $[\alpha]$, and it remains to see how far this agreement is diminished when only solutions of low concentration are employed in the calculations, as is the case with bodies of slight solubility.

Experiments of this kind have been made with right and left turpentine, nicotine, and ethyl tartrate (Landolt).[1]

In the following observations, which for purpose of illustration are given in full, the angles of rotation were found mostly by aid of the Wild polaristrobometer and as the means of ten single observations. The normal temperature of 20° employed was secured by jacketed tubes, the densities d are reduced to water at 4° as standard.[2]

I. Left Turpentine Oil

The French oil with boiling-point 160° to 162° was used and the rotation found in two tubes of different length:

d_4^{20}	l in dm	a^{20}	$[\alpha]_D^{20°}$
0.8629	0.9992	−31.91	−37.00
"	2.1979	−70.20	−37.02
		Mean,	−37.01

a. Mixtures with Alcohol.

The specific gravity of the alcohol used was, $d_4^{20} = 0.7957$:

Mixture No	Turpentine oil p	Alcohol q	d_4^{20}	a for $l = 2.1979$ dm	$[\alpha]_D^{20}$
I	90.05	9.95	0.8556	−62.72°	−37.04°
II	69.94	30.06	0.8392	−48.05	−37.25
III	49.97	50.03	0.8254	−34.04	−37.55
IV	29.97	70.03	0.8127	−20.29	−37.90
V	10.01	89.99	0.8011	−6.78	−38.49

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[1] Landolt. Ann. Chem. (Liebig), 189, 311 (1877).

[2] In the following tables all the numbers, which in the original paper were carried out to four places of decimals for p and q, to five places for d and to three places for a and $[\alpha]$, have been shortened. In consequence a recalculation of $[\alpha]$ might lead in some instances to values differing by one or two units in the last decimal from those now given. But this is of no consequence for the present purpose.

b. Mixtures with Benzene

The benzene used had a boiling-point of 80.4° and a specific gravity, $d_4^{20} = 0.8803$:

Mixture No	Turpentine oil p	Benzene q	d_4^{20}	α for $l = 2.1979$ dm	$[\alpha]_D^{20}$
I	89.92	10.08	0.8634	−63.47°	−37.19°
II	77.93	22.07	0.8644	−55.50	−37.49
III	65.06	34.94	0.8656	−46.79	−37.80
IV	51.05	48.95	0.8677	−37.18	−38.18
V	36.90	63.10	0.8705	−27.20	−38.52
VI	22.06	77.94	0.8738	−17.21	−39.03
VII	9.98	90.02	0.8771	− 7.59	−39.45

c. Mixtures with Acetic Acid

The acetic acid used had a density, $d_4^{20} = 1.0502$, corresponding to 99.8 to 99.9 per cent. of real acid.

Mixture No	Turpentine oil p	Acetic acid q	d_4^{20}	α for $l = 2.1979$ dm.	$[\alpha]_D^{20}$
I	90.16	9.84	0.8757	−64.46°	−37.15°
II	78.07	21.93	0.8917	−57.23	−37.41
III	64.86	35.14	0.9116	−49.24	−37.89
IV	50.97	49.03	0.9353	−40.27	−38.43
V	22.96	77.04	0.9918	−19.86	−39.67
VI	9.84	90.16	1.0233	− 8.90	−40.22

As the above observations show, the specific rotation of the turpentine increases in all cases with increase in the amount of inactive solvent q, and in the curves shown in the graphic illustration (Fig. 16) that for acetic acid ascends the most rapidly, that for benzene less, and that for alcohol the least. The curvature of these is not great, but they differ too much from a straight line to permit the application of the formula $[\alpha] = A + Bq$. If the constant A is determined from two mixtures, values are found which are always smaller than the specific rotation of the pure turpentine oil (37.01), and which depart the more widely from this, the more dilute the solutions are that are used in the observations. This is shown, for example, by the following figures:

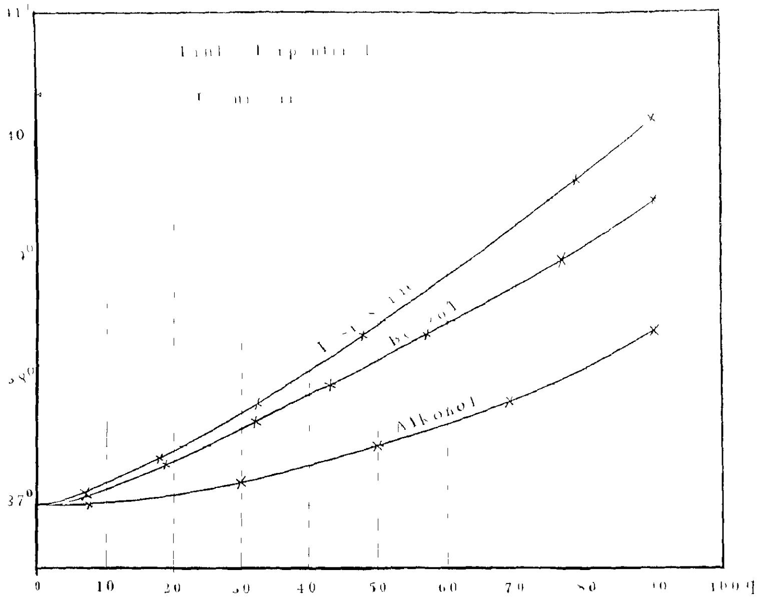

Fig 16

From the mixtures with alcohol	There results $A =$	Deviation from 37 01	Extrapolation Per cent
I and II	36.93	— 0 08	10
II " III	36 79	— 0 22	30
III " IV	36 66	— 0 35	50
IV " V	35 87	— 1 14	70

If, on the other hand, the formula $[\alpha] = A + Bq + Cq^2$, be used and the constants be calculated from solutions with the smallest, a mean, and the largest value for q, there results for A a number which is very near the specific rotation of the pure turpentine oil, and further, the formula agrees in a very satisfactory manner with the whole determined curve from $q = 10$ to 90

There follow from the mixtures with

a. Alcohol, calculated from solutions I, III, V,

$$[\alpha]_D = 36.97 + 0.004816\ q + 0.0001331\ q^2.$$

b. Benzene, calculated from solutions I, IV, VII,

$$[\alpha]_D = 36.97 + 0.021531\ q + 0.0000667\ q^2.$$

c. Acetic Acid, calculated from solutions I, IV, VI,

$$[\alpha]_D = 36.89 + 0.024553\, q + 0.0001369\, q^2.$$

These formulas give the following interpolation values:

Solutions in	Mixture No.	q	$[\alpha]_D$ Observed.	$[\alpha]_D$ Calculated	Cal − Obs.
Alcohol....	II	30.06	37.25°	37.24°	0.01°
	IV	70.03	37.90	37.96	+ 0.06
Benzene ...	II	22.07	37.49	37.48	0.01
	III	34.94	37.80	37.80	0.00
	V	63.10	38.52	38.59	+ 0.07
	VI	77.04	39.03	39.03	0.00
Acetic acid.	II	21.93	37.41	37.50	+ 0.09
	III	35.14	37.89	37.93	+ 0.04
	V	77.04	39.67	39.60	0.07

If we employ only the dilute solutions in calculating the constant *A*, by the three-term formulas, deviations of the following kind are found.

From the mixtures with		There results $A =$	Deviation from 37.01	Extrapolation Per cent
Alcohol ...	II, IV, V	37.20°	+ 0.19°	30
	III, IV, V	35.13	1.88	50
Benzene...	III, V, VI	37.26	+ 0.25	35
	V, VI, VII	35.42	1.59	63
Acetic acid.	II, IV, VI	36.65	0.36	22
	IV, V, VI	36.00	1.01	49

The deviations from the true value amount then to 1° to 2° as soon as the mixtures contain more than about 50 per cent of inactive liquid.

II. Right Turpentine Oil.

The American oil used showed at a temperature of 21° the following densities and rotations, the last being found by two different polariscopes:

d_4^{21}	Apparatus	l	α_D	$[\alpha]_D^{21}$
0.9108	I	2.1990 dm	+ 28.35°	+ 14.16°
	II	2.1990 "	+ 28.315	+ 14.14
				Mean, 14.15

Mixtures with Alcohol.

The following mixtures were made:

Mixture No.	Turpentine oil. p	Alcohol. q	d_4^{20}	α for $l = 2.199$ dm.	$[\alpha]_D^{20}$
I	73.09	26.91	0.8765	+ 20.42°	+ 14.50°
II	47.51	52.49	0.8464	+ 13.08	+ 14.79
III	22.24	77.76	0.8186	+ 6.04	+ 15.10

Also here with increasing dilution, a slight increase in the specific rotation follows, and the graphic illustration (Fig. 17) shows that the three points lie almost exactly in a straight line. The simple formula $[\alpha] = A + Bq$ can therefore be applied, for the constants in which we have

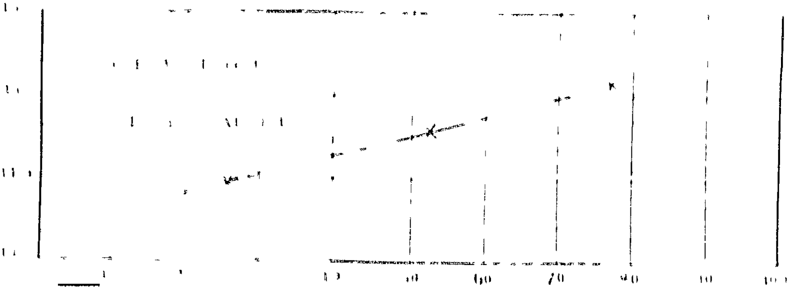

Fig. 17

From I and II	$A = 14.19$	$B = +0.01142$
" II " III	14.15	0.01215
" I " III	14.18	0.01178

The values found for A agree, accordingly, very closely with those found by direct observation of the turpentine oil (in the mean 14.15°).

The mean of the above values for A and B gives this formula:

$$[\alpha]_D^{20} = 14.17 + 0.01178\,q.$$

III. *Nicotine (Left-Rotating).*

A preparation secured by distilling the commercial product in an atmosphere of hydrogen was tested as to purity, and was found to have a boiling-point of 246.6°–246.8° at 745 mm.

The rotation, as well as that of the mixtures given later, w determined by means of the Wild polaristrobometer, and w

d_4^{20}	l	α_D^{20}	$[\alpha]_D^{20}$
1.0110	0.9992 dm	− 163.20°	− 161.55°

a. Mixtures with Alcohol

The alcohol used had a specific gravity, d_4^{20} 0.7957.

Mixture No.	Nicotine. p	Alcohol. q	d_4^{20}	α for l 0.9992	$[\alpha]_D^{20}$
I	90.09	9.91	0.9884	141.16°	158.6
II	74.93	25.07	0.9536	− 110.62	154.9
III	59.93	40.07	0.9200	− 83.63	151.7
IV	45.08	54.92	0.8875	− 59.49	148.8
V	30.03	69.97	0.8554	− 37.32	145.4
VI	14.96	85.04	0.8251	— 17.46	141.6

As shown, the specific rotation of the nicotine decrease the dilution with alcohol increases. The graphic construc (Fig. 18) leads to a straight line with slight variations to eit side, and, corresponding with this, we obtain for the const of the formula $[\alpha] = A + Bq$, almost the same values w ever mixtures are made the bases of the calculation:

From mixtures	There results A =	Deviation from 161.55.	Extrapolation. Per cent.	B
I and III	160.90°	0.65°	10	0.22
II " IV	160.06	1.49	25	0.20
III " V	160.31	1.24	40	0.21
IV " VI	161.96	+ 0.41	55	0.23
I " VI	160.90	− 0.65	10	0.22

We find therefore, from dilute solutions also, results fo which, in view of the strong rotation, agree very well wit value found for $[\alpha]$ (= − 161.55) from the pure nico From the means of A and B we obtain the formula

$$[\alpha]_D^{20} = -160.83 - 0.2224\,q,$$

which leads to the following interpolation results:

Mixture No.	q	$[\alpha]$ Observed.	$[\alpha]$ Calculated.	Cal.—Obs.
I	9.91	158.65°	158.63°	− 0.02
II	25.07	154.92	155.26	+ 0.34
III	40.07	151.78	151.92	+ 0.14
IV	54.92	148.81	148.62	− 0.19
V	69.97	145.42	145.27	− 0.15
VI	85.04	141.60	141.92	+ 0.32

b. Mixtures with Water

Mixture No.	Nicotine. p	Water. q	$d_4^{20°}$ [1]	l in dm.	α_D^{20}	$[\alpha]_D^{20}$
I	89.92	10.08	1.0267	0.9992	123.47°	133.85°
II	78.39	21.61	1.0353	0.9992	88.82	109.53
III	65.90	34.10	1.0401	0.9992	64.54	94.24
IV	53.48	46.52	1.0365	0.9992	47.95	86.58
V	34.29	65.71	1.0228	0.4982	14.11	80.78
VI	17.68	82.32	1.0116	0.4982	6.855	76.94
VII	16.34	83.66	1.0096	0.4982	6.317	76.88
VIII	8.97	91.03	1.0047	0.9992	6.804	75.53

From the table it appears that the specific rotation of the nicotine suffers at first a very sharp decrease with increase in the amount of water added, which later becomes gradually less. The strongly bowed curve (Fig. 18) is a limb of a hyperbola and it is not possible by use of the formula $[\alpha] = A + Bq + Cq^2$, even with addition of a fourth or fifth member, to reach a satisfactory agreement with the observations. The specific rotation of the pure nicotine may be found, even approximately, only by calculation from the numbers obtained by observations on the strongest solutions. There results, for example:

From mixtures	I, II, III	I, IV, VII.	IV, V, VIII.
A	163.17	153.00	141.16

If it is desired to express the whole curve, an equation of some other form must be employed, as, for example, the following which contains five constants:

$$[\alpha] = 115.019 - 1.70607\,q + \sqrt{2140.8 - 108.867\,q + 2.5572\,q^2}.$$

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[1] The specific gravity of the mixtures increases at first with the increase in the water, reaches a maximum with mixture III, and then decreases.

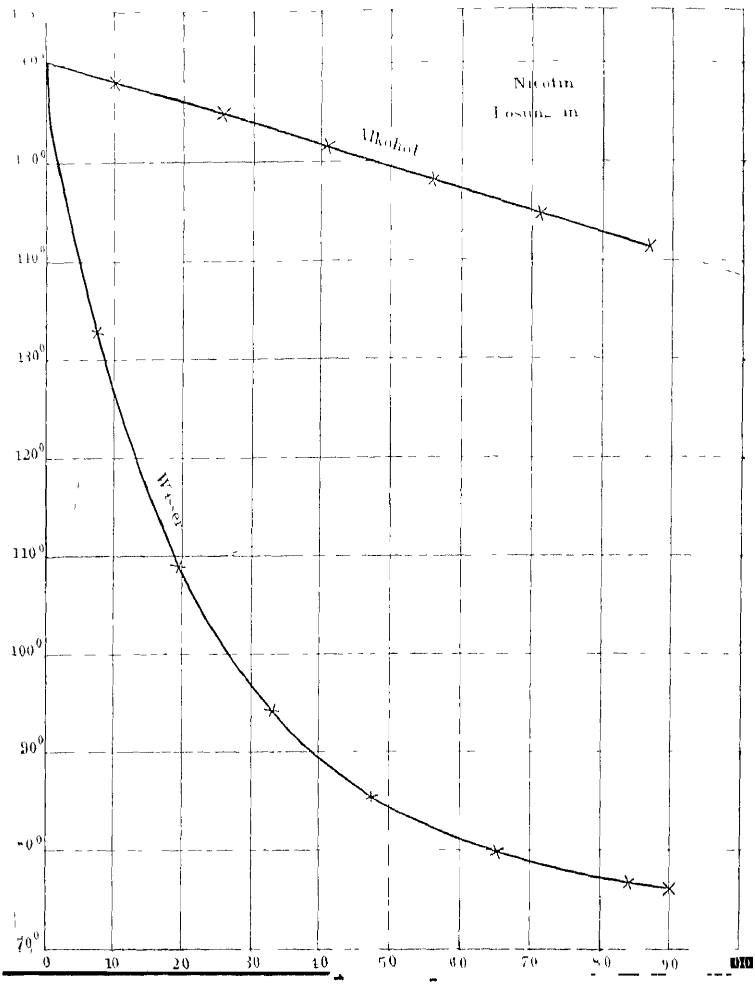

Fig 18

Mixture No	q	$[\alpha]$ Observed	$[\alpha]$ Calculated	Cal —Obs
I	10.08	133.85°	133.92°	+ 0.07
II	21.61	109.53	109.49	0.04
III	34.10	94.24	94.28	+ 0.04
IV	46.52	86.58	86.74	+ 0.16
V	65.71	80.78	80.56	0.22
VI	82.31	76.94	77.08	+ 0.14
VII	83.66	76.88	76.84	− 0.04
VIII	91.03	75.53	75.56	+ 0.03

For pure nicotine ($q = 0$) the above formula gives $[\alpha] = 161.29°$, instead of the observed 161.55°.

For $q = 100$ $[\alpha] = 74.13°$; by dilution, nicotine suffers therefore a decrease in its specific rotation which amounts to more than half its original value.

IV. Ethyl Dextrotartrate.

The preparation used, which was not quite pure, gave the following specific rotation :[1]

d_4^{20}	l	α_D^{20}	$[\alpha]_D^{20}$
1.1989	0.9992 dm	9.32°	8.29°
	0.4982 "	4.97	8.33
		Mean,	8.31

a. Mixtures with Alcohol.

Specific gravity of the alcohol $d_4^{20} = 0.7962$:

Mixture No.	Ethyl tartrate p	Alcohol q	d_4^{20}	α for $l = 2.20$ dm	$[\alpha]_D^{20}$
I	77.98	22.02	1.0837	16.315°	8.78°
II	35.74	64.26	0.9989	6.87	9.62
III	22.33	77.67	0.8634	4.17	9.85

The specific rotation increases gradually, therefore, with the amount of alcohol, and the change may be represented by a curve of very slight curvature (Fig. 19) which almost coincides with a straight line. For the formula $[\alpha] = A + Bq$ there follows :

From mixtures		A	B
I and II		8.34	+0.0198
" "	II " III	8.52	0.0170
" "	I " III	8.36	0.0192

and in the mean,

$$[\alpha]_D = 8.41 + 0.0187\,q.$$

The formula with three constants gives $A = 8.27°$.

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[1] The imperfect purity of the substance employed was without consequence for this investigation. One could just as well take a mixture of the active body with any inactive substance as a basis, and determine how exactly the original specific rotation might be found from observations on solutions.

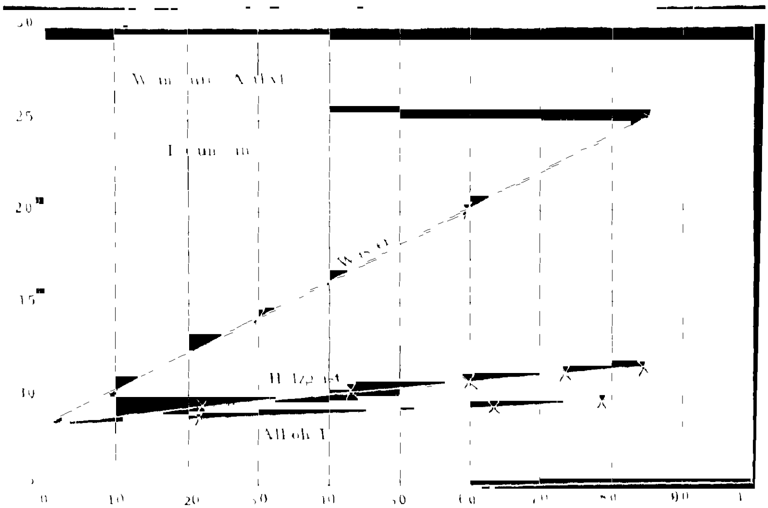

Fig. 19

b. *Mixtures with Methyl Alcohol*

Mixture No	Ethyl tartrate p	Methylalcohol q	d_4^{20}	α for $l = 2$ 198 dm	$[\alpha]_D^{20}$
I	77 46	22.54	1.0882	17 88°	9.65°
II	56.65	43 35	1 0007	12.97	10.41
III	39.92	60.08	0.9381	8.98	10.92
IV	26.97	73.03	0.8946	5.87	11.07
V	15.31	84 69	0.8568	3 23	11.21

The slight change which the specific rotation of the ethy tartrate suffers by reason of the presence of the methyl alcohc is not quite proportional to the dilution but may be represente by a curve, at first rather strongly and later less strongl inclined (This does not show in the figure because of th small scale on which it is drawn.) From mixtures I, II, an III we have

$$[\alpha]_D = 8.42 + 0.0625\, q - 0.0003479\, q^2,$$

the constant A agreeing fairly well with the rotation of th original ethyl tartrate. If we use for the calculation th dilute solutions III, IV, and V we obtain $A = 10.25$, which differs rather widely from the true value of 8.31.

c. *Mixtures with Water*

These were polarized immediately after making.

Mixture No.	Ethyl tartrate. p	Water. q	d^{20}_{4}	l in dm.	α	$[\alpha]^{20}_{D}$
I	69.69	30.31	1.1508	2.198	24.68°	14.00°
II	39.82	60.18	1.0884	2.199	19.27	20.22
III	13.89	86.11	1.0292	2.198	7.92	25.20

The very strong increase in the specific rotation of the tartrate on addition of water is almost proportional to the amount of the latter added. For the constants of the formula, $[\alpha] = A + Bq$ we obtain:

From mixtures I and II		$A = 7.69$	$B = + 0.2082$
"	" II " III	8.66	0.1920
"	" I " III	7.92	0.2007

and in the mean,

$$[\alpha]_D = 8.09 + 0.2003q.$$

The marked deviation in the constant A from the specific rotation of the original tartrate (8.31) may be a result of the beginning saponification of the latter. After forty-eight hours, the above solutions gave rotations smaller by 0.1 to 0.2°.

From the above investigations with turpentine, nicotine, and ethyl tartrate as well as from many other experiments, the following relations have been established:

1. The specific rotation of an active body on increasing dilution with an indifferent inactive liquid suffers no sudden change, but a gradual progressive alteration. Whether the latter is in the nature of an increase or decrease depends on the nature of the active body; thus, oil of turpentine and ethyl tartrate on being mixed with different solvents show always an increase, while nicotine and camphor (for which experiments follow in §53) show a decrease in the specific rotation. But on one and the same active body different solvents act in very different degrees, so that if the results were represented graphically curves would be obtained, which, starting from the origin of coordinates, representing the rotation of the pure substance, would radiate from each other

The weaker, therefore, a solution of an active substance is, the greater is the deviation of its specific rotation from that which it shows in pure condition. The whole of the changes which have been found here may be shown by calculating from the interpolation formulas, the limits for $q = 0$ (pure substance) and $q = 100$ (maximum of dilution) With the bodies investigated we obtain the following numbers

Active substance	Solvent	$[\alpha]_D$ Of the pure substance $q = 0$	$[\alpha]_D$ For maximum dilution $q = 100$	Difference
Turpentine oil (left-rotating)	alcohol	36.97°	38.79°	+ 1.82°
	benzene	36.97	39.79	+ 2.82
	acetic acid	36.89	40.72	+ 3.83
Turpentine oil (right-rotating)	alcohol	14.17	15.35	+ 1.18
Nicotine (left-rotating)	alcohol	160.83	138.59	− 22.24
	water	161.29	74.13	− 87.16
Ethyl tartrate (right-rotating)	alcohol	8.27	10.19	+ 1.92
	wood alcohol	8.42	11.19	+ 2.77
	water	8.09	28.12	+ 20.03

It appears, therefore, that the specific rotation of an active substance is changed by different solvents to very differen degrees

2 *From the specific rotation of a number of solutions it is possibl to calculate that of the pure substance.* The degree of certainty with which this is true is different for different substances and is dependent on the following conditions *a* Upon th extent of the changes made in the specific rotation by th inactive solvent. The greater these are, the more unfavorabl in general, are the conditions for calculation (as in the case o nicotine for example). *b.* Upon the manner in which thes changes take place by increase in the amount of inactiv

solvent, that is, upon whether they may be represented by a straight line, or by one more or less strongly curved. *c.* Upon the concentrations of the solutions used. The stronger these are the greater is the certainty in the calculations. The above investigations show that in cases where the formula, $[\alpha] = A + Bq$, is applicable, the constant A agrees accurately with the true rotation of the pure substance (or within a few tenths of a degree), when the strongest solution contains about 50 per cent. of active substance. If, on the other hand, the use of the formula, $[\alpha] = A + Bq + Cq^2$, is necessary, variations of more than a degree can appear if solutions containing less than 80 per cent of active substance are taken as the basis of calculation.

3 In the calculation of the original specific rotation of a substance, the same value is always obtained independently of which indifferent liquid is employed as a solvent The numbers found for the active bodies investigated (the constants A) are given below

I TURPENTINE OIL (LEFT)

Directly observed	$[\alpha]_D$	37.01°	....
Calculated from the mixtures with alcohol	"	36.97	—0.04°
" " " " " benzene	"	36.97	—0.04
" " " " " acetic acid	"	36.89	+0.12

II TURPENTINE OIL (RIGHT).

Directly observed	"	14.15	....
Calculated from the mixtures with alcohol	"	14.17	—0.02

III NICOTINE (LEFT)

Directly observed	"	161.55	....
Calculated from the mixtures with alcohol	"	160.83	—0.72
" " " " " water	"	161.29	—0.26

IV. ETHYL TARTRATE (RIGHT)

Directly observed	"	8.31	....
Calculated from the mixtures with alcohol	"	8.27	—0.04
" " " " " methyl alcohol	"	8.42	+0.11
" " " " " water	"	8.09	—0.22

The differences found are so small that they evidently must be results of errors of observation.

4. In the comparison of the rotations of different dissolved bodies, only those values may be used which hold for the pure *substances, that is, the constants A.* If specific rotations which embrace the changes due to the solvents be taken as the basis for comparison, possible relations will appear, the less distinctly, the weaker the solutions from which the numbers were obtained.

In certain cases the constant A can have, besides, a different meaning from that of simply expressing the original rotation of the single molecules of the active body. This would be true when the active substance forms definite compounds with the solvent, or when the active molecules unite to form aggregations which as such possess rotation. See § 63 and 64.

53. **Determination of the True Specific Rotation of Solid Active Substances.**—The method to be employed here is suggested by what has just been given. First of all it is essential to prepare solutions of the greatest possible concentration, and as the nature of the inactive solvent is immaterial one must be chosen which best permits the fulfilling of this requirement With the aid of such a solvent it is necessary to prepare at least three solutions of different concentrations and to determine their rotating power. If the relation between the specific rotation, $[\alpha]$, and the percentage amount of the solvent, q, be expressed graphically and it is seen that the three points lie in a straight line, that is, that $[\alpha]$ changes directly with q, then the constant, A, calculated from the formula $[\alpha] = A + Bq$ will express the specific rotation of the pure substance But if the middle point lies higher or lower than the others then a larger number of solutions must be investigated in order to establish the curve as completely as possible, for which then a corresponding interpolation formula ($[\alpha] = A + Bq + Cq^2$, or analogous one) is to be calculated. It is also possible to obtain by the graphic method, that is by prolonging the curve obtained to the abscissa $q = 0$, a value which approximates more or less closely to the specific rotation of the pure substance.

It must be understood that numbers obtained by such extrapolations must be received with caution. To secure greater certainty it must not be neglected to carry out the investigation with several different solvents; if the values so found for the constant *A* agree among themselves closely the mean of these will be taken as the sought-for specific rotation of the substance, but if they do not agree the whole calculation must be rejected.

In consequence of their conditions of solubility the calculation of the specific rotation of the original substances is made very difficult in many cases. According to experience as referred to above it will be possible to obtain reliable numbers only in such instances where solutions may be made with at least 50 per cent. of active substance, and where further the curve of rotation obtained does not vary too much from a straight line. With all difficultly soluble bodies there is no prospect of finding the true specific rotation in pure condition.

As an illustration of obtaining the true specific rotation of an active solid substance, a series of experiments with ordinary camphor may be given here. A number of solutions in different liquids were made and from these the following figures secured by observation.

Solvent	No of solution	Camphor p	Solvent q	d_4^{20}	α_D^{20} for $l = 2$ 1979 dm	$[\alpha]_D^{20}$
Acetic acid	I	65 2519	34 7481	0 98983	72 117°	50 801°
	II	39 7183	60 2817	1 01128	41 652	47 181
	III	15 8819	84 1181	1 03389	15 887	44 021
Acetic ether.	I	53 7260	46 2740	0 93269	58 492	53.109
	II	34.5489	65 4511	0 91987	36 520	52.283
	III	14 9221	85 0779	0 90686	15 290	51 408
Mono-chloracetic ether.	I	54.2184	45.7816	1 04206	65 356	52 631
	II	31.3990	68 6010	1 08670	38 340	51 123
	III	14 2332	85 7668	1 12243	17 543	49 961
Benzene.	I	63 1250	36 8750	0.93067	63 575	49 236
	II	49 6359	50 3641	0 91920	47 097	46.966
	III	24 3169	75 6831	0.89910	20 638	42.948
Dimethyl-aniline.	I	57.1519	42 8481	0 95997	59.533	49 370
	II	36 0428	63 9572	0 95914	35 151	46.263
	III	15 1028	84 8972	0 95813	13 708	43.101
Methyl alcohol	I	49 3866	50 6134	0 88093	46 840	48 996
	II	30 3154	69 6846	0 85318	26 820	47.179
	III	11 2590	88 7410	0 82700	9 382	45.844
Alcohol.	I	54 7281	45 2719	0 88021	50 634	47.823
	II	49 8142	50.1858	0 87194	44.806	46.934
	III	30 1620	69.8380	0 84031	25 013	44.901
	IV	15 0920	84.9080	0 81752	11 840	43.661
	V	9 6883	90.3117	0.80943	7.378	42.806

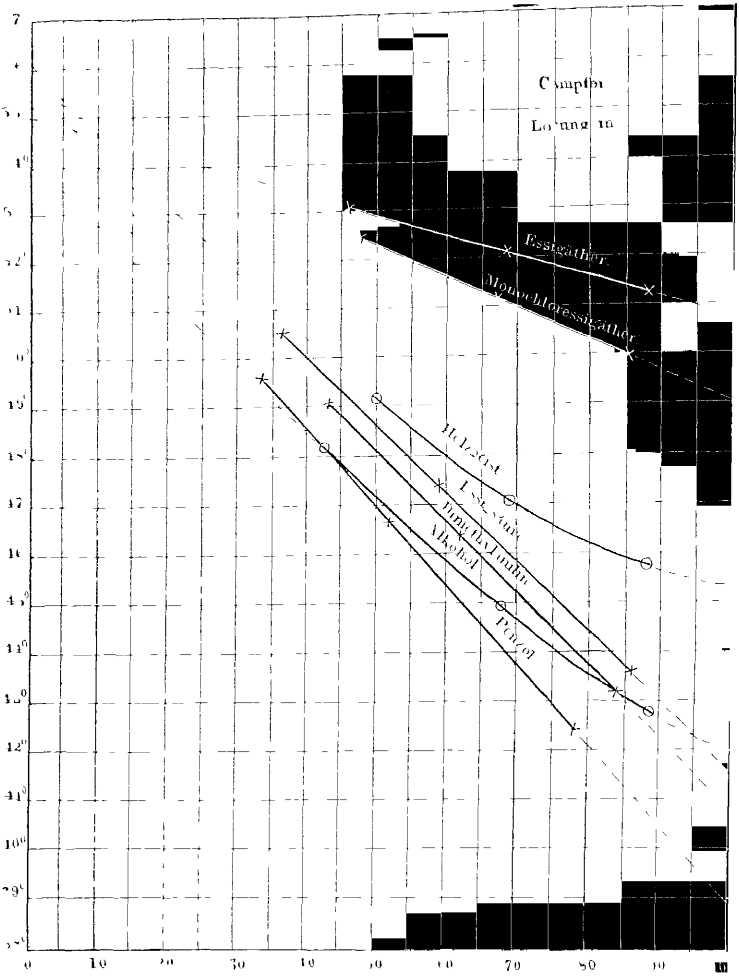

Fig 20

The specific rotations with all these solutions decreases the amount of solvent increases, but in very different degre with different inactive solvents The graphic illustration (Fi 20) shows that these changes may be represented almo exactly by straight lines when as solvents acetic acid, acet ether, monochloracetic ether, benzene and dimethylaniline are used; the formula, $[\alpha] = A + Bq$, is then applicable in these cases. But with ethyl alcohol and methyl alcohol the deviation from the straight line is too large, and the formula $[\alpha] = A + Bq + Cq^2$, was used for the calculations.

The following table contains: (1), the values obtained for the constants A and B from the different solutions; (2), the mean interpolation formulas calculated from these; (3), the calculated specific rotations of the solutions employed, obtained by these formulas, and the differences between these and the observation values given in the preceding table.

	1				3		
	$[\alpha] = A - Bq$						
Solvent	Calculation from solutions	A	B	Means	Solution	$[\alpha]_D$ calculated	Difference from observations
Acetic acid	I and II II and III I and III	55 73 55 17 55.58	0 1418 0 1326 0.1373	$[\alpha]_D = 55\ 49 - 0\ 13723\, q$	I II III	50 72 47 22 43.95	− 0 39 + 0 04 − 0 07
Acetic ether	I and II II and III I and III	55 11 55.21 55 14	0 04307 0 04458 0 04384	$[\alpha]_D = 55\ 15 - 0\ 04383\, q$	I II III	53 12 52.28 51.41	+ 0 01 0 00 0 00
Monochloracetic ether	I and II II and III I and III	55 65 55 77 55 69	0 06608 0 06769 0 06677	$[\alpha]_D = 55.70 - 0\ 06685\, q$	I II III	52.64 51.12 49.97	+ 0 01 0 00 + 0.01
Benzene	I and II II and III I and III	55 45 54 96 55 21	0 1683 0.1587 0.1620	$[\alpha]_D = 55\ 21 - 0\ 1630\, q$	I II III	49.19 47 00 42 87	− 0 05 + 0 03 − 0 08
Dimethylaniline	I and II II and III I and III	55.68 55 92 55 76	0 1472 0.1510 0.1491	$[\alpha]_D = 55\ 78 - 0\ 1491\, q$	I II III	49 40 46 25 43 13	+ 0.03 − 0 01 + 0.03
Methyl alcohol	I II III	$[\alpha]_D = 56\ 15 - 0.1749\, q + 0\ 0006617\, q^2$					
Alcohol	I III V	$[\alpha]_D = 54.38 - 0.1614\, q + 0\ 0003690\, q^2$[1]			II IV	47.21 43.33	+ 0.28 − 0 33

---

[1] The formula $[\alpha] = A + \frac{Bq}{C+q}$ gives $[\alpha]_D = 54.83 - \frac{42\ 879\, q}{231\ 82 + q}$.

If we compare with each other the values obtained for the constant A, from the different solutions an agreement is found which, in consideration of the great extrapolations necessary (from $q = 0$, amounting to 25 to 50 per cent), must be considered as a very close one; we can look upon the mean of these numbers, therefore, as representing the true specific rotation of the pure camphor. The values for B, depending on the solvent, vary on the contrary, very greatly. If we calculate from the formulas the specific rotations for the two limits, $q = 0$ and $q = 100$, the following results are obtained, from which may be seen to what extent the different solvents influence the rotating power of camphor ·

Solvent	$[\alpha]_D$ for $q = 0$ $= A_D$ Pure substance	$[\alpha]_D$ for $q = 100$ Infinite dilution	Total change
Acetic acid....	55 5°	41 8°	13 7°
Acetic ether..........	55.2	50.8	4 4
Monochloracetic ether	55 7	49 0	6 7
Benzene	55 2	38 9	16 3
Dimethylaniline	55 8	40.9	14 9
Methyl alcohol.......	56 2	45 3	10 9
Alcohol	54 4	41 9	12 5

From the numbers obtained we have finally as the original rotation of camphor at 20°,

$$[\alpha]_D = 55.4°,$$

with a mean error of ± 0 4°.

54. Slight Changes in Specific Rotation by Variations in Concentration.—Such are observed, as will be shown later in the chapter in which changes in the rotation are more fully discussed, in cases in which an action of the solvent on the active body is as far as possible excluded, and where, therefore, molecular aggregation, dissociation or hydrolysis, etc., can not take place. A body of this kind is cane-sugar for which Tollens[1] and also Schmitz[2] have shown by accurate investigations that the specific rotation undergoes a slight but regular increase with decrease in the concentration. The observations of

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[1] Tollens Ber. d. chem Ges, 10, 1403 (1877)

[2] Schmitz *Ibid*, 10, 1414.

Schmitz which were carried out by methods described in Part IV, using a Wild and also a half shadow polarimeter, are given here as an illustration of careful experiments :

No	Grams sugar in 100 grams solution p	Grams sugar in 100 cc. solution $c=pd$	Specific gravity d_4^{20}	α_D^{20} for $l = 2$ dm	$[\alpha]_D^{20}$ Observed.	Calculated.	Difference Obs.—Cal.
I	64 978	85.543	1.31650	112 268°	65.620°	65.619°	+ 0.001°
II	54 964	69 108	1 25732	91 066	65.888	65.911	— 0.023
III	39.978	47 039	1.17664	62 348	66.272	66.242	+ 0.030
IV	25 002	27 594	1.10367	36 670	66 441	66.448	— 0.007
V	16.993	18 144	1.06777	24 128	66 448	66.506	— 0.018
VI	10 000	10 382	1 03820	13.824	66 574	66.528	+ 0.046
VII	4 998	5 087	1 01787	6.776	66.609	66.526	— 0.083

In calculating the constants of the formula $[\alpha] = A + Bq + Cq^2$ the solutions I, III and V were used, then II, IV and VI and the mean taken. The following equations were obtained with relation to the percentage amount of sugar, p, and that of the water, $100 - p = q$, which, as seen from the table, agree very well with the observations

$$[\alpha]_D^{20} = 66\ 510 + 0\ 004504\, p - 0.0002805\, p^2$$
$$[\alpha]_D^{20} = 64.156 + 0.051596\, q - 0\ 0002805\, q^2$$

The investigations of Tollens[1] which embraced an examination of seventeen solutions, with $p = 3.8$ to $69\ 2$ led to these formulas·

$$[\alpha]_D^{20} = 66.386 + 0.015035\, p - 0.0003986\, p^2$$
$$[\alpha]_D^{20} = 63\ 904 + 0.064686\, q - 0.0003986\, q^2$$

By a different method of calculation from the observations of Tollens, Th. Thomsen[2] derived this equation,

$$[\alpha]_D^{20} = 64\ 190 + 0.055212\, q - 0.0003134\, q^2$$

the constant A in which (64.190) agrees very well with that of Schmitz, 64.156. We can therefore look upon these numbers as giving with considerable certainty the specific rotation of cane-sugar in amorphous dry condition, as the concentrations of the solutions were carried to an extreme degree.

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[1] Tollens. Ber. d. chem. Ges., 10, 1410 ; 17, 1757

[2] Th Thomsen *Ibid*, 14, 1651

Experiments which were carried out by Biot[1] and later by Tollens[2] on the specific rotation of cane-sugar in fused condition led to uncertain results because of beginning decomposition, and can not be used therefore to control the above results.

55. Specific Rotation in Very Dilute Solutions.—If the rotating power of an active body is changed by some effect of the solvent, it might appear possible that this action would come to an end after a certain decrease in the concentration had been passed, and consequently that, with still further dilution, the specific rotation would remain constant. Such an effect could be produced, for example, by electrolytic dissociation.

Investigations of this kind offer, in general, very considerable experimental difficulties, inasmuch as the errors of observation assume a great importance in connection with the small values of the angles of rotation. Thus far, but a few substances, partial or non-electrolytes, have been tested in very dilute solutions with reference to their rotating power.

Tartaric Acid.—The specific rotation of aqueous solutions increases with the dilution and according to Arndtsen[3] may be represented, for amounts of water from $q = 50$ to 95 per cent., by the formula:

$$[\alpha]_D^{24} = 1.950 + 0.13030\,q$$

That this increase in the specific rotation goes still further by increase of q from 95.28 to 99.65 has been shown by experiments undertaken by Pribram.[4] But this no longer corresponds to a linear formula as pointed out by Bremer,[5] and it appears that $[\alpha]$ increases more rapidly than it does in concentrated solutions.

Cane-Sugar.—A number of investigations have been carried out on the rotation of this substance in very dilute solutions. The formula of Tollens (§54) for concentrations from $p = 69$ to 4,

$$[\alpha]_D^{20} = 66.386 + 0.015035\,p - 0.0003986\,p^2,$$

gives at first an increase in the specific rotation when the concentration is diminished from 69 per cent., and reaches a maximum at $p = 18.86$ per cent. (66.528°); there is then a decrease, so that for $p = 1.1$, $[\alpha] = 66.402°$. Direct experiments with dilute solutions[1] with $p = 10$ to 1 per cent. of sugar gave irregular values between $[\alpha] = 66.499°$ and 66.276°, the variations in which from those calculated by the above formula lie within the errors of observations, but show in general a slight decrease Pribram[2] in dropping from $p = 3.659$ to 0.222 in five steps found a continuous decrease in the specific rotation from $[\alpha]_D^{20} = 66\ 531°$ to 66.213°. On the other hand, Nasini and Villavecchia[3] observed for five concentrations lying between $p = 1.253$ and 0 824, a regular increase from $[\alpha]_D^{20} = 67.37°$ to 68 24°. The results are therefore contradictory; but for practical use, the Tollens formula may be looked upon as satisfactory for all concentrations.

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[1] Biot: Mém. de l'Acad., **13**, 131 (1835).

[2] Tollens: Ber. d. chem. Ges., **10**, 1413 (1877).

[3] Arndtsen: Ann. chim. phys., [3], **54**, 403; Pogg. Ann., **105**, 312.

[4] Pribram: Ber. d. chem. Ges., **20**, 1846.

[5] Bremer: Rec. Trav. chim. Pays-Bas, **6**, 258.

Dextrose.—According to Tollens[4] the formulas,

Anhydrous dextrose ..... $[\alpha]_D^{20} = 52.50 + 0\ 018796p + 0\ 0005168p^2$

Dextrose hydrate .... $[\alpha]_D^{20} = 47\ 73 + 0.015534p + 0\ 0003883p^2$,

derived from concentrated solutions, satisfy the results of observation down to a decreased concentration of $p = 1$.

It has not been certainly shown, therefore, with any of the above substances that the character of the curve expressing the dependence of the specific rotation on the concentration undergoes a change for very great dilutions. A case, on the other hand, where the behavior is essentially different will be discussed in the following paragraph. (See Nicotine.)

56. **A Minimum Value of Specific Rotation.**—This peculiar phenomenon has been recognized in the following cases:

Nicotine, dissolved in water. As already shown in §52, the specific rotation decreases in a very marked degree as the dilution increases, and this was followed to $q = 91$ per cent., at which point the original rotation of the nicotine, $[\alpha]_D^{20} = -161.55°$ had sunk to -75.53. Pribram[5] first noticed that when q is increased from 96 to 99 per cent., an increase in the rotation from $[\alpha]_D^{20} = -77.03°$ to $-79.32'$ follows This behavior has been more fully investigated by Hein,[1] who determined the point of minimal rotation; he employed a sample of nicotine with $[\alpha]_D^{20} = -164.00°$ and examined eight dilute solutions at temperatures of 5°, 15° and 20°. These tests were combined with a series of cryoscopic molecular weight determinations of nicotine ($C_{10}H_{14}N_2 = 162$) in the same or nearly same concentrations The values obtained are the following:

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[1] Tollens Ber d. chem. Ges., 17, 1751.

[2] Pribram · *Ibid*, 20, 1848

[3] Nasini and Villavecchia · Wied. Beib, 16, 366.

[4] Tollens: Ber d chem. Ges, 17, 2238

[5] Pribram. *Ibid*, 20, 1848

In 100 parts by weight		$[\alpha]_D^{5}$	$[\alpha]_D^{15}$	$[\alpha]_D^{20}$	Molecular weight determination		
Nicotine p	Water q				Nicotine in 100 parts of solution	Molecular weight found	Variation from 162
15 592	84 408	$-$ 73 39°	$-$ 76 18°	$-$ 77 59°	13 736	275	113
11 206	88 794	73 05	75 96	77 01	11 512	261	99
10 258	89 742	72.78*	75 59*	76.89	8 307	235	73
8 307	91 693	73.07	75 76	76 84*	5.700	209	47
5 700	94 300	73 81	76 00	76 96	3.016	180	18
3 016	96 984	74 46	76 27	77 25	2 042	168	6
2 042	97.958	74 74	76 35	77.32	1 225	165	3
1 061	98 939	74 79	76 83	77 66	0.346	163	1

It appears, therefore, that at the temperatures of 5° and 15° a minimum specific rotation (marked *) occurs when the amount of nicotine is about 10 per cent., and at a temperature of 20° this minimum is found in the solution of about 8 per cent strength. From the molecular weight determinations it is seen that nicotine in very dilute solutions is present as a normal molecule while in the more concentrated, hydrates and, likely, molecular aggregations exist. To these a much lower rotating power must be ascribed than to the pure nicotine, but if these are broken up by increasing dilution, as suggested by the decrease in the molecular weight, more and more fresh nicotine appears by which the decrease in the specific rotation is gradually arrested and finally an increase in the rotation

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[1] Hein: "Ueber das specifische Drehungsvermögen und das Moleculargewicht des Nicotins in Lösungen" Inaug Diss Berlin, 1896 (Investigations carried out in the author's laboratory.)

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must follow. In this manner it may be possible to explain the occurrence of the minimum in the case in hand.

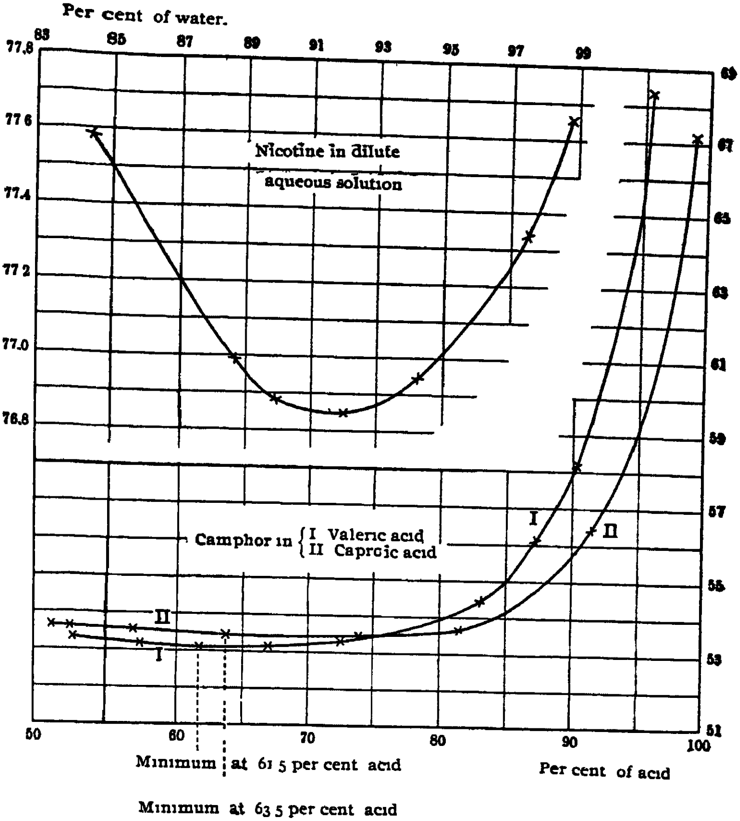

Fig 21

In Fig. 21, above, the rotation for 20° is graphically shown.

Camphor, dissolved in isovaleric or caproic acid. The following solutions have been investigated by H. Vogel[1] and a minimum rotation (*) found for large concentrations :

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[1] H. Vogel. "Ueber das optische Drehungsvermögen des Camphers." Inaug Diss. Berlin (Investigations carried out in the author's laboratory)

Isovaleric acid			Caproic acid		
Camphor p	Val acid. q	$[\alpha]_D^{20}$	Camphor p	Capr acid. q	$[\alpha]_D^{20}$
52.37	47 63	+53.43°	49 84	50 16	+ 53.67°
46.71	53.29	53 29	47.88	52.12	53 63
43.03	56 97	53 16	43.30	56.70	53 46
38 55	61.45	53.10*	36.48	63 52	53 22*
36.71	63.29	53 20	26.19	73.81	53.42
32.22	66.78	53.28	18.49	81 51	53.70
27.06	72 94	53.40	8 53	91.47	56.51
18.28	81.72	54 51	2.31	97.69	67.19
12 63	87.37	56.02	...	....	. ..
9 46	90 54	58.17	....	. ..	. ..
4 36	95 64	68 41	..	...	....
3 05	96.95	76.44	....	....	...

As seen from the above numbers, and also from the graphic illustration in Fig. 21, the specific rotation of the camphor decreases at first in very slight amount, from the point of greatest concentration on, with an increase in the percentage of acid, but reaches a minimum when the amount of isovaleric acid is 61 45 per cent or the amount of caproic acid is 63 52 per cent Then a slow increase in the rotation begins, and only after considerable dilution does a sudden and marked change appear. Corresponding to the minimum point in the rotation there is no simple molecular proportion between the amounts of acid and camphor. The dependence of the specific rotation on the amount of acid can be represented, according to Vogel, by the following formulas:

Isovaleric acid. .... $[\alpha]_D^{20} = 57.15 - 0.12572\,q + 0.001000\,q^2$

Caproic acid .... $[\alpha]_D^{20} = 58\ 90 - 0.16846\,q + 0.001279\,q^2$

Solutions of camphor in other fatty acids do not exhibit the appearance of a minimum or a great increase in the specific rotation with strong dilution, but' $[\alpha]$ decreases regularly with increased addition of acid, as was true with the solvents described in § 53. Vogel gives the following observations·

Formic acid		Acetic acid		Propionic acid		N. Butyric acid	
q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$
35.89	+ 39.93°	47.25	+ 49.37°	60.92	+ 50.53°	49.10	+ 52.49°
49.11	35.08	61.16	47.20	69.40	49.70	63.07	51.35
57.68	32.38	65.65	46.60	76.93	48.98	68.39	50.94
65.62	29.85	70.40	45.93	86.30	48.34	76.76	50.07
75.95	26.91	80.78	44.24	....	....	88.34	49.67
79.56	26.03	83.58	43.87	....	....	93.44	49.56
....	....	91.50	43.36	...	....	....	....

The effect of these fatty acids on the original rotation of the camphor (+ 55.4°) is decreased, as easily seen, with increased molecular weight of the acids. It is not clear upon what the peculiar behavior of the valeric and caproic acids depends.

57. Reversal in the Direction of Rotation by Change in Concentration.—In the case of bodies whose specific rotations decrease with increase in the amount of solvent, it may happen that the rotation will sink to zero and then, with increased dilution, rise in the opposite direction.

This behavior was first noticed by Schneider[1] in aqueous solutions of ordinary malic acid and some of its salts, for which the following results were obtained.

Malic acid		Sodium acid malate		Sodium malate		Barium malate	
q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$	q	$[\alpha]_D^{20}$
29.88	+ 3.34°	39.45	+ 0.15°	34.47	+ 4.72°	90.62	+ 1.81°
40.01	+ 2.31	50.46	— 1.71	44.74	+ 2.15	91.50	+ 1.61
50.13	+ 1.38	60.28	— 3.27	51.21	+ 0.50	95.01	+ 0.54
53.53	+ 1.00	69.98	— 4.26	53.16	— 0.16	98.04	— 0.11
62.47	+ 0.17	79.81	— 5.57	57.78	— 1.26	....	....
63.34	+ 0.09	80.05	— 5.64	66.09	— 3.43	....	...
64.74	— 0.04	....	....	70.01	— 4.34	....	....
70.31	— 0.34	....	....	74.73	— 5.28	....	....
70.94	— 0.63	....	....	85.34	— 6.98	....	....
83.35	— 1.58	....	....	94.73	— 8.39	....	....
85.65	— 1.73	....	....	....	....	....	....
91.68	— 2.30	....	....	....	....	....	....

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[1] G. H. Schneider: Ann. Chem. (Liebig), 207, 257

The relation of the specific rotation to the amount of wate q, can be expressed by the formulas,

Malic acid................ $[\alpha]_D^{20} = 5.89 - 0.0896\,q$
Sodium acid malate........ $[\alpha]_D^{20} = 9.37 - 0.2791\,q + 0.001152\,q^2$
Sodium malate .... $[\alpha]_D^{20} = 15.20 - 0.3322\,q + 0.000814\,q^2$,

from which by taking $A + Bq + Cq^2 = 0$, the values of are obtained at which the solution becomes inactive.

	Malic acid	Sodium acid malate	Sodium malate
$q =$	65.76	40.25	52.57

A change in the direction of rotation does not occur wi the other alkali malates; they all exhibit increasing le rotation with changes in concentration from greatest strengt to extreme dilution.

The causes on which these changes possibly depend a explained in §63.

The same phenomenon has been observed with *l*-sodiu lactate dissolved in alcohol (Purdie and Walker),[1] and wit aqueous solutions of the barium salts of *d*-methoxysuccin acid (Purdie and Marshall)[2] and *d*-ethoxysuccinic acid (Purd and Walker)[3] This may be seen from the following table i which c is the number of grams of active substance dissolve in 100 cc. of solution At the foot of the table are given th concentrations corresponding to the inactive points

l-Sodium lactate (in alcohol)		*d*-Barium methoxysuccinate (in water)		*d*-Barium ethoxysuccinat (in water)	
c	$[\alpha]_D^{10}$	c	$[\alpha]_D^{18}$	c	$[\alpha]_D^{1}$
23.21	− 2.28°	26.13	− 14.27°	21.48	− 4.37
19.79	− 2.22	12.42	− 7.36	10.77	+ 2.46
11.20	− 0.80	5.75	− 2.21	4.56	+ 6.37
9.29	− 0.48	1.15	+ 3.16	..	....
7.47	+ 1.34	....	...	....	....
5.60	+ 2.50	....	.. .	....	....
2.24	+ 8.93	....	....	....	....
1.12	+ 10.36	..	....	....	....
0.56	+ 20.53	....	...	....	....
8.81	0	3.85	0	14.63	0

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[1] Purdie and Walker. J Chem Soc, 67, 631 In the original, the values ($\frac{M}{100}[\alpha]$ are given

[2] Purdie and Marshall J Chem. Soc., 63, 227

[3] Purdie and Walker *Ibid*, 63, 235

A change of sign takes place with the following substances, investigated by Freundler,[1] when they are brought from the pure condition ($c = 100$) into solution:

d-Ethyl diacetyltartrate in chloroform		*d*-Propyl dicaproyltartrate			
		In bromoform		In benzene.	
c	$[\alpha]_D$	c	$[\alpha]_D$	c	$[\alpha]_D$
100	+ 5.0°	100	+ 2.2°	100	+ 2.2°
50	— 5.3	23.16	— 5.2	19.59	— 2.0
40	— 5.9	5.88	— 7.1	10.83	— 3.6
30	— 6.5	2.39	— 8.0	5.45	— 4.3
20	— 7.1	....	...	1.54	— 5.4
10	— 7.5	...	..	....	..
5	— 8.8	.	..	....	..
2.5	— 10.0	...	...	....	...

58. **Increase or Decrease in Specific Rotation with Increasing Dilution of Solutions.**—As shown by the examples thus far given with some substances there is an increase, and with others a decrease in the specific rotation as the amount of solvent is increased. In order to show at a glance the relations found, a number of observations are given in diagram form, the increase or decrease of rotation being indicated by the direction of arrows. The solvents used are given in parentheses.[2]

A Increase in Rotation.	—	0°	+
1. Active Acids and Their Salts.			
d-Tartaric acid (water)			→
d-Sodium tartrate, neutral (water)			→
d-Thallium-potassium (Na, Li, NH_4) tartrate (water)			→
d-Ethylenediamine tartrate (water)			→
d-Ethyl tartrate (water, methyl-ethyl alcohol)			→
d-Diacetyltartaric acid anhydride (acetone, benzene)			→
d-Dibenzoyltartaric acid anhydride (acetone, alcohol)			→
d-Dibenzoyltartaric acid (alcohol)	←		
d-Dibenzoyltartaric acid, dimethyl and diethyl esters (alcohol)	←		
d-Propyldicaproyl tartrate (carbon disulphide)			→

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[1] Freundler Ann chim phys, [7], 4, 252

[2] The observations on which the table is based are given in Part VI.

1. Active Acids and Their Salts. (*Continued*)	— 0° +	
d-Lactate of K, Na, Cd (aqueous alcohol)	←	
l- " " K, Na, Li, Ca, Zn (aqueous alcohol)		→
Glucuronic acid and K-salt (water)		→
Podocarpate of sodium (water)		→
Cholalate of Na and K (water)		→
2. Active Bases and Their Salts.		
Quinidine (alcohol)		→
" hydrochloride, sulphate (water, alcohol)		→
Cinchonine (alcohol + chloroform)		→
" hydrochloride, sulphate (water, alcohol)		→
Apocinchonine hydrochloride (water)		→
Quinamine (alcohol, ether, chloroform)		→
Conquinamine (alcohol, benzene)		→
Quinicine oxalate (alcohol + chloroform)		→
Laudanosine (alcohol)		→
l-Cocaine hydrochloride (alcohol)		→
Cupreine hydrochloride, hydrobromide, sulphate (water)	←	
Quinine anhydride and hydrate (alcohol)	←	
" hydrochloride, sulphate (water, alcohol)	←	
Cinchonidine (alcohol)	←	
" hydrochloride, sulphate (water)	←	
Hydrocinchonidine hydrochloride (water)	←	
Morphine hydrochloride, sulphate (water)	←	
Pseudomorphine hydrochloride (water)	←	
Thebaine hydrochloride (water)	←	
Strychnine (chloroform)	←	
Brucine (chloroform)	←	
l-Cocaine (chloroform)	←	
3. Sugar Group.		
Cane sugar (water)		→
Maltose (water)		→
Salicin (water)	←	
4. Aromatic Substances.		
d-Pinene (alcohol)		→
l- " (alcohol, acetic acid, benzene)	←	
l-Menthol (alcohol, acetic acid, benzene)	←	
α-Nitrocamphor (benzene)	←	
B. Decrease in Rotation		
1 Active Acids and Their Salts.		
d-Potassium tartrate, neutral (water)		←
d-Sodium acid tartrate (water)		←

1. Active Acids and Their Salts (*Continued.*)	— 0°	+
d-Sodium borotartrate (water)		←
d-Diacetyltartaric acid (water, alcohol)	→	
d-Di-1-butyldiacetyl tartrate (alcohol)	→	
d-Mandelic acid (water)		←
l-Mandelic acid (water)	→	
d-Camphoric acid (alcohol, acetone, acetic acid)		←
d- " " salts (water)		←
Quinate of Ba, Sr, Ca, Mg, Zn (water)	→	
Shikiminic acid (water)	→	
Sodium santoninate (water)	→	
Cholalic acid (alcohol)		←
2 Active Bases and Their Salts.		
d-Conine (alcohol, benzene)		←
d- " hydrochloride, hydrobromide, acetate (alcohol)		←
Nicotine (water, alcohols, aniline, toluidine)	→	
" hydrochloride, sulphate, acetate (water)		←
Benzoylcinchonine (alcohol)	→	
β-Isocinchonine (alcohol)	→	
" hydrochloride (water)	→	
Hyoscyamine (alcohol)	→	
3. Sugar Group.		
Dextrose (water)		←
Xylose (water)		←
Rhamnose (water)		←
Levulose (water)	→	
Phloridzin (alcohol)	→	
4 Aromatic Substances		
d-Camphor (alcohols, fatty acids, ethyl acetate, benzene, dimethyl aniline)		←
Cholesterol (chloroform)	→	

In general the following points are shown by the above table:

1. With the active acids and their salts there is observed an increase as well as a decrease in specific rotation; bodies as closely related as potassium tartrate and sodium tartrate show opposite behaviors.

2. With the alkaloids and their salts increase in the rotation is the usual phenomenon.

3. Among bodies of the sugar group, the monosaccharides appear to show a decrease and the disaccharides an increase.

Further, it is to be noticed that different solvents exert the same action on many of the above bodies.

An explanation of these phenomena, as far as it is now possible, will be given in §61 to §66.

B. Dependence of the Specific Rotation on the Nature of the Solvent.

59. If equal weights of an active body are dissolved in different inactive liquids, the specific rotation can assume very different values depending on the manner in which the solvent behaves with the substance. Several illustrations of this have been given in former chapters, a number of observations follow in which this variation comes strongly into view.

Freundler[1] found the following figures for some substituted tartaric acid esters in solutions of concentration, $c = 5$ to 6:

	N Propyl diacetyl-tartrate $[\alpha]_D$	N Propyl dibutyryl-tartrate $[\alpha]_D$	N Propyl dicaproyl-tartrate $[\alpha]_D$
Pure ester.	+ 13.3°	+ 5.2°	+ 2.2°
Solution in:			
Carbon disulphide....	+ 36.7	+ 28.8	+ 27.5
Methyl alcohol	+ 12.1	+ 9.3	+ 5.4
Acetone.......	+ 10.4	+ 7.2	+ 5.3
Ethyl alcohol.....	+ 9.6	+ 6.3	+ 3.6
Ethylene bromide	+ 8.6	+ 5.5	+ 2.4
Butyrone	+ 8.5	+ 3.8	+ 1.3
Ethylidene chloride	+ 6.4	+ 2.7	...
Monochlorethylidene chloride ..	+ 6.4	+ 2.3	+ 0.6
Ligroin	+ 6.2	+ 2.6	− 0.2
Methylene chloride	+ 5.7	+ 2.8	..
Ethylene chloride....	+ 5.3	+ 3.1	+ 0.3
Methyl iodide...........	+ 4.7	+ 1.7	
Carbon tetrachloride	+ 3.8	+ 0.6	− 1.9
Toluene................	+ 3.4	+ 0.6	− 2.1
Methylene bromide	+ 1.7	+ 2.4	...
Benzene	+ 1.2	− 1.4	− 4.3
Chloroform	+ 1.2	− 0.1	− 4.0
Bromoform	− 2.6	− 3.8	− 7.1

It is apparent that the specific rotations of the original substances are sometimes increased, and sometimes diminished by the inactive liquids, and further, that the order in which the solvents stand with reference to their action is almost the same for the three substances.

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[1] Freundler Compt rend., 117, 556; Ann chim phys., [7], 4, 244.

Even bodies which exhibit but slight changes in specific rotation, such as cane-sugar, show quite appreciable deviations when dissolved in different liquids. Tollens[1] investigated solutions of the following composition

10 parts sugar + 90 parts water		$[\alpha]_D = +66.67°$
10 " " + 23 " " + 67 parts	ethyl alcohol	" $= +66.83$
	acetone	" $= +67.40$
	methyl alcohol	" $= +68.63$

It may also happen that a change in the direction of rotation can take place by application of different solvents. Illustrations of this have been shown by tables already given, and others are furnished by substances described below.

d-Tartaric Acid, which rotates to the right when dissolved in water, exhibits left-rotation when dissolved in a mixture of acetone and ether (Landolt).[2] Pribram[3] found very marked variations by use of the following liquids in which the amount of substance dissolved was always 5 grams to make 100 cc.

Solvent	$[\alpha]^{20}_D$
Water	$+14.40°$
Alcohol	$+3.79$
Equal vols. of alcohol and mononitrobenzene	$+3.17$
" " " " " nitroethane	$+3.09$
" " " " " mononitrotoluene	-0.69
" " " " " ethyl bromide	-3.62
" " " " " benzene	-4.11
" " " " " toluene	-6.19
" " " " " xylene	-6.52
" " " " " cymene	-7.91
" " " " " monochlorbenzene	-8.09

As far as explanations of this behavior are possible they will be given in the chapter on the causes of changes in specific rotation, § 61 to 65.

C. Dependence of the Specific Rotation on the Temperature.

60. Increase of temperature affects different active bodies in

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[1] Tollens. Ber. d. chem Ges, 13, 2303

[2] Landolt. *Ibid.*, 13, 2332

[3] Pribram *Ibid*, 22, 6.

different ways; with some there is an increase, with others decrease in the rotation and in different degrees

Among *active crystals*, as remarked in § 44, only quartz an sodium chlorate have been investigated in this directio With both, an increase in the rotation follows on warmin The change here is, therefore, the reverse of that in the ord nary refraction of light which is diminished by increase temperature.

Liquid Active Bodies.—If such a substance is contained in a observation tube, which, to accommodate expansion, is fu nished with a lateral opening, then on application of heat t density must decrease and consequently the number of mol cules in the active column, causing a diminution of the ang of rotation. But, on the other hand, the length of the tu has increased which exerts an action of the opposite kind. I calculating the specific rotation, $[\alpha] = \frac{\alpha}{l\,d}$, these influenc are eliminated if density and length of tube are found for t same temperature at which the rotation is determined, and case these alone come into question the values for $[\alpha]$ shou remain constant. But according to experience this is not qui true in the case of any known body, and it follows that he must exert some special effect on optical activity.

On the effect of temperature on bodies which are in ther selves liquids we have but few observations.

Increase in specific rotation with increase in temperature h been found, for example, in the following bodies.

a. *Nicotine*, left-rotating.—According to investigations Landolt[1] which are here given in full to illustrate the chang in the different factors observed, there were found:

Temp. t	d_4	l	α_D	$[\alpha]_D$
10.2°	1.01837	99.914[2]	— 163.776°	— 160.96°
20.0	1.01101	99.923	— 163.204	— 161.55
30 0	1.00373	99.932[2]	— 162.450	— 161.96

It is seen that while the angle of rotation has becor smaller with increasing temperature, the specific rotation, on the contrary, has grown. The increase is small and amounts to about 0.05 for 1°.

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[1] Landolt Ann Chem. (Liebig), 189, 319 (1877).

[2] Calculated from the length measured at 20° by aid of the coefficient of exp sion, 0 0000086

b. The left-rotating *esters of glyceric acid and diacetyl glyceric acid* show also an increase in $[\alpha]_D$, according to Frankland and MacGregor,[1] and for ordinary temperatures the following amounts for 1°:

Glycerate of	methyl	0.036°
	ethyl	0.033
Diacetyl-glycerate of	methyl	0.073
	ethyl	0.067
	N-propyl	0.063
Diacetyl-glycerate of	isopropyl	0.065°
	isobutyl	0.054
	N-heptyl	0.067
	N-octyl	0.043

c. For the right-rotating *esters of tartaric acid*, Pictet[2] found:

	Temperature	
	20°	100°
Methyl tartrate	$[\alpha]_D = +$ 2.14	$[\alpha]_D = +$ 6.00
Ethyl tartrate	" $= +$ 7.66	" $= +$ 13.29
N-propyl tartrate	" $= +$ 12.44	" $= +$ 17.11
I-propyl tartrate	" $= +$ 14.89	" $= +$ 18.82

If the increase in $[\alpha]$ was proportional to the change in temperature it amounted to about 0.05 to 0.07 for 1°.

d. An increase in the angle of rotation has been found in the following bodies:

Right-rotating isobutyl isoamyloxide (Le Bel[3] and Colson),[4]
" di-isoamyl oxide .... (Colson),[4]
" methyl isoamyloxide .... (Colson),[4]
" amyl acetate .... (Colson),[5]
Left-rotating methyl lactate .... (Le Bel).[3]

With reference to the question whether the change in rotation could follow from polymerization with lower temperature, LeBel[6] observes that according to the investigations of Ramsay (1) ethyl tartrate possesses the simple molecular weight for all temperatures, (2) the same is true of isobutylamyl oxide between — 23° and + 125°, (3) that, on the other hand, propyl

[1] Frankland and MacGregor J Chem Soc, 65, 760 (1894)

[2] Pictet Arch de Genève, [3], 7, 82 (1882)

[3] LeBel: Compt rend, 118, 916 (1894)

[4] Colson: *Ibid.*, 116, 319 (1893).

[5] Colson: *Ibid.*, 119, 65, 1894. From the papers of LeBel and Colson, it is not clear whether the data refer to the observed angle of rotation or to the specific rotation.

[6] LeBel, Compt rend., 118, 916; 119, 226 (1894).

glycol has the double molecular weight above 100° and t quadruple weight at the ordinary temperature, without sho ing any change in activity corresponding to this polymerizatio This supposed cause appears therefore to be insufficient.

A decrease in specific rotation with elevation of temperatu was observed by Gernez[1] in several essential oils. It was fou that the decrease could be expressed by the following formul holding from 0° to 150°:

Right turpentine oil..... $[\alpha]_D = 36.61 - 0.004437\,t$
Orange oil.............. $[\alpha]_D = 115.31 - 0.1237\,t - 0.0_4 16\,t^2$
Bitter orange oil .... $[\alpha]_D = 118.55 - 0.1175\,t - 0.0_2 216\,t^2$

The decrease goes still further when the temperature of t boiling-point is passed and the body becomes a vapor (see § On the other hand, as Gernez found, the dispersion suffers marked change by heat.

Dissolved Active Bodies.—As experiment has shown, w these also there may be a change, not only in the observ angle of rotation, but in the specific rotation, which m undergo either an increase or decrease by change in tempe ture. In the following table in which bodies already m tioned are included (and marked with an *) all the kno relations are given

CHANGE IN THE SPECIFIC ROTATION WITH INCREASED TEMPERATU

− 0° +

Increase in left rotation ←	← Decrease in right rotation
*Nicotine	*Right turpentine oil
*Esters of glyceric acid	*Orange oil
*Esters of diacetylglyceric acid	*Bitter orange oil
Malic acid in dilute aqueous solution	Malic acid in strong solution
	Cane-sugar in water
	Milk-sugar " "
	Maltose " "
	Galactose " "
	Arabinose " "
	Rhamnose " "
	Cinchonicine in alcohol
	Quinidine " "
	Quinidine sulphate in water
	Tartar emetic " "

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[1] Gernez: Ann. de l'Ecole normal, 1, 1 (1864)

[2] The extent of the changes in the rotation of the different substances, as f observations reach, will be given in the chapter on "Constants of Rotation."

— 0° +	
Decrease in left rotation →	→ Increase in right rotation
Turpentine oil	*Isobutylamyl oxide
Fructose (levulose) in water	*Methylisoamyl oxide
Invert sugar " "	*Diisoamyl oxide
Saccharin " "	*Amyl acetate
Mandelic acid " "	*Methyl lactate
Sodium santoninate " "	*Tartaric acid esters
Quinine in alcohol	Tartaric acid in water
Quinine sulphate and disulphate in alcohol	Alkali tartrates in water
Cinchonidine in alcohol	Glucuronic acid " "
Thebaine " "	Xylose " "
Glutin " water	N-propyl dibutyryl tartrate in monobromethylidene bromide

A change in the direction of rotation by elevation of temperature, when a point of inactivity is passed is shown in the following table ·

	— 0° +
Aspartic acid in water............	←
Malic acid " "	←
Tartaric acid " "	→
Invert sugar " "	→

On the last four substances we have the following more complete data

Aspartic Acid.—Aqueous solutions which are perfectly free from other acids as well as from alkalies, exhibit right rotation at the ordinary temperature. But, as found by Ellen Cook,[1] this decreases with elevation of temperature, and passes finally into increasing left rotation, the point of inactivity being passed at 75° The following specific rotations for white light, $[\alpha]_j$ (converted into $[\alpha]_D$ by multiplication with 0.89), were found by use of supersaturated solutions. The values of the concentration, c, were found by determination of the density at the temperatures at which the rotations were observed.

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[1] Ellen P. Cook · Ber d chem Ges, 30, 294.

Solution. No	Amount p	Temp t	Specific gravity d_4^t	Concentr. c	Observed α_t	Specific rotatio	
						$[\alpha]_t$	$[\alpha$
I	0.528	20°	1 00185	0.531	+ 0.103°	+ 4.90°	+ 4
II	1.872	32	1 0043	1.880	+ 0 320	+ 4.25	+ 3
II	1.872	40	1.0015	1.875	+ 0.255	+ 3.40	+ 3.
II	1.872	50	1.0004	1 873	+ 0.130	+ 1 74	+ 1.
II	1 872	60	0.9917	1 857	+ 0.102	+ 1.37	+ 1.
II	1.872	75	0.9821	1 838	0	0	0
II	1.872	77	0.9800	1 835	— 0 050	— 0 68	— 0
II	1.872	80	0.9777	1.830	— 0 062	— 0 85	— 0.
II	1 872	90	0.9747	1 825	— 0 155	— 2.12	— 1.

Malic Acid (*common*).—Concentrated solutions show ri rotation which decreases with elevation of temperature; dil solutions are levorotatory and more strongly, the higher temperature. In solutions of a certain strength right rotat appears at a low temperature, and left rotation at a high te perature and the point of inactivity changes with alterati in the percentage amount, p, of acid. This behavior, wh is shown by neutral sodium malate also, can be seen in following observations of Th. Thomsen:[1]

	p	$t = 10°$	$t = 20°$	$t =$
Malic acid....	53 75	$[\alpha]_D = + 2.52$	$[\alpha]_D = + 1.73$	$[\alpha]_D = +$
	0 44	+ 1 31	+ 0.54	—
	28.67	+ 0 33	— 0 35	—
	21.65	— 0 44	— 0.90	—
Sodium malate.	42.75	+ 0.38	— 0.89	—

Tartaric Acid.—In examining tartaric acid melted wit little water in a glass vessel with parallel walls, Biot[2] obser at first right rotation which, with falling temperature, decrea and on solidification passed into left rotation.

The right rotation characteristic of aqueous solutions tartaric acid increases with heat in a marked degree, as appe from the following observations of Krecke:[3]

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[1] Th Thomsen Ber. d chem Ges, **15**, 441.

[2] Biot Ann chim phys., [3], **59**, 206, § 11 (1860)

[3] Krecke Arch. Néerland, **7**, 97 (1872)

Temp	Amount of tartaric acid in solution		
	40 Per cent.	20 Per cent.	10 Per cent
0°	$[\alpha]_D = +$ 5.53	$[\alpha]_D = +$ 8.66	$[\alpha]_D = +$ 9.95
10	7.49	9.96	10.94
20	8.32	11.57	12.25
30	9.62	12.49	13.93
40	11.03	13.65	15.68
50	12.27	15.01	17.11
60	12.63	16.18	18.31
70	13.38	17.16	19.42
80	14.27	18.40	20.72
90	15.91	19.99	22.22
100	17.66	21.48	23.79

Of the salts of tartaric acid, according to Krecke, disodium and sodium potassium tartrate show a slight increase, but potassium antimonyl tartrate a decrease in rotation by elevation of temperature.

Invert Sugar.—As Tuchschmid[1] found, an aqueous solution with 17.21 grams in 100 cc. shows a diminution of its left rotation with elevation of temperature, according to the formula $[\alpha]^t_D = -27.9 + 0.32\,t$. Therefore, the rotation must become zero at 87.2°, to pass into right rotation at a still higher temperature. In agreement with this, v. Lippmann[2] found the point of inactivity to be at 87.8°, and Casamajor[3] at 88°

If alcohol is added to the invert sugar, which causes a decrease in the left rotation, the change in direction follows on moderately warming. If, for example, a solution of 19 grams of cane-sugar in 15 cc of water and 5 cc. of glacial acetic acid is inverted by heating in the water-bath, and diluted afterwards to 100 cc with absolute alcohol, the liquid which now contains 20 grams of invert sugar, shows the following angles of rotation:

t	20°	30°	40°	50°	60
α_D for 2 dm.	$-1.9°$	$-0.9°$	$+0.2°$	$+1.3°$	$+2.2°$

The point of inactivity is therefore found to be about 38° (Landolt).[4]

The change in the direction of rotation may be explained when the active substance consists of two oppositely rotating components which are affected to different extents by heat. This is the case with invert sugar. As first shown by Dubrunfaut,[1] and later more particularly by Hönig and Jesser,[2] the rotating power of levulose decreases rapidly on warming (α_D for 1° C. about 0.67°), while that of dextrose is but slightly altered; the direction of rotation of the latter becomes then gradually apparent. As another case, Aignan[3] has shown that a mixture of left turpentine and right camphor in benzene may change its direction of rotation with elevation of temperature, and with different kinds of light at different degrees. The numbers given in the following table are the observed angles of rotation in a 2 dm. tube:

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[1] Tuchschmid J prakt Chem, [2], 2, 235 (1870)
[2] v. Lippmann . Ber. d. chem. Ges, 13, 1822 (1880)
[3] Casamajor: Wied. Beib., (1879), 804.
[4] Landolt Ber. d. chem. Ges., 13, 2335 (1880)

Temperature	Red light	Yellow light	Green light
+ 13°	− 2.62	− 0.72	+ 2.40
33 to 38°	− 1.53	− 0.40	+ 4.08
50 " 51	− 0.83	+ 1.50	+ 5.10
61 " 62	− 0.35	+ 1.98	+ 5.55
65 " 72	+ 0.18	+ 2.67	+ 5.90
81 " 90	+ 0.57	+ 3.00	+ 6.72

Finally, it is of interest to determine, whether, with the same substance, elevation of temperature and increasing dilution exert like changes in the specific rotation. Thus far, but few bodies have been studied in both directions, and with several of them, the alterations observed have been very slight. What has been found is tabulated below.

a. Corresponding Changes in the specific rotation through increasing dilution or elevation of temperature occur in:

	− 0°	+
d-Tartaric acid in water.............		→
d-Tartrates and esters in water.......		→
Malic acid and malates " "	←	
Glucuronic acid " "		→
Sodium santoninate " "	→	
l-Mandelic acid " "	→	
Levulose " "	→	
Rhamnose " "		←
Galactose " "		←

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[1] Dubrunfaut Compt. rend., 42, 901 (1856)

[2] Hönig and Jesser Zeit Ver. f. Rubenzucker-Ind., (1888), p 1039

[3] Aignan Compt rend., 116, 725, (1893)

b. Opposite Effects are observed in the following cases:

	Increasing temperature — 0° +		Increasing dilution. — 0° +	
Quinine in alcohol	→		←	
Quinine sulphate in alcohol or water	→		←	
Cinchonidine "	→		←	
Quinidine "		←		→
Quinidine sulphate in water		←		→
Nicotine in water or alcohol	←		→	
Cane-sugar in water		←		→
Maltose "		←		→
Xylose "		→		←
d-Turpentine in alcohol		←		→
l- " " benzene, acetic acid	→		←	

It is evident, therefore, that increased temperature and dilution have sometimes the same and sometimes the opposite actions and that no definite regularity is apparent with respect to the nature of the substances examined Those cases in which an explanation of this behavior is in any degree possible will be discussed in the following chapter.

D. Causes of the Changes in Specific Rotation.

The many variations which are exhibited in the specific rotation of dissolved substances depend, according to the nature of the substances, on essentially different causes, and all changes which are in general possible with solutions, as electrolytic dissociation, formation or breaking up of molecular aggregations, hydrolysis and other less clearly defined effects may come into play Besides this the explanation of the phenomenon is made difficult by the fact that of the nature of concentrated solutions almost nothing is known. Up to the present time the following data have been accumulated with reference to each one of these influences

61. a. Electrolytic Dissociation in Aqueous Solutions.—In 1873 in the examination of a number of neutral salts of tartaric acid, it was remarked that they agreed very closely with each other in molecular rotation, from which it was clear that differences in the metals combined had but little effect, and this not in any relation with the atomic weight (Landolt).[1] Oudemans[2] appeared to find in solutions of cinchona alkaloids in different dilute acids which were added in increasing molecular weights, a difference in the effects of these additions, but in 1879, in pursuing further investigations with quinamine, he found that the rotation of this alkaloid remains almost unchanged in whatever acid it is dissolved.[3] The law then stated, "*the specific rotation of the alkaloids is modified in th same manner by different acids, provided the salts formed represent the same condition of saturation of the alkaloid by the acid,*' was later confirmed by Oudemans[4] in the study of quinidine amine and by Tykociner[5] with brucine, strychnine, morphin and codeine. Finally, Oudemans[6] showed that the rule hold good for the active acids as he found that podocarpic aci and quinic acid, after saturation with different bases, or in th form of dilute salt solutions, retain nearly the same rotatin powers.

The following table contains some of the results referred t the rotation for equal molecular weights being expressed b (M) for salts or by $[\alpha]_D$ for the active group

Tartrates (Landolt)		Quinates (Oudemans)			Quinamine (Oudemans)	Strychni (Tykociner)
					1 mol of acid to 1 m of base	
In 100 cc. 7 69 grams tartaric acid	$[M]^{20}_D$ of the salt	In 100 cc 2 6 grams quinic acid $C_7H_{12}O_6$	$[\alpha]_D$ of the acid.	Acids	In 100 cc 1.56 grams base $[\alpha]^{16}_D$ of the base	In 100 c 0 84 gra base $[\alpha]^{20}_D$ of the ba
$Li_2 . C_4H_4O_6$	+58 1°	$K.C_7H_{11}O_6$	−48.8°	HCl	+114.4°	−34.1
$(NH_4)_2$ "	63 0	Na "	48.9	HNO_3	116 5	34.1
Na_2 "	59.9	NH_4 "	47.9	$HClO_3$	116.1	...
K_2 "	64.4	$Ba(C_7H_{11}O_6)_2$	46.6	H_2SO_4	116.4	35.
Na NH_4 "	61.7	Sr "	48.7	H_3PO_4	117 3	34.
$K.NH_4$ "	63.8	Ca "	48.7	H_3AsO_4	....	33.
K.Na "	62.3	Mg "	47.8	CH_2O_2	114.7	34.
K.AsO "	58.8	Zn "	51.0	$C_2H_4O_2$	116.2	34.
$K.C_2H_5$ "	64.6			$C_2H_2O_4$	118.1	33.
$Ba1/2C_2H_5$ "	63.0			$C_6H_8O_7$	....	33.
Mg "	61.7					

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[1] Landolt · Ber d. chem Ges , **6**, 1077 (1873).

[2] Oudemans · Ann Chem. (Liebig), **182**, 33, 58 (1876). Arch Néerland, **10**, 193.

[3] Oudemans : Ann. Chem (Liebig), **197**, 48, 66 (1879). Arch. Néerland, **15**, See further, Rec trav. Chim Pays-Bas, **1**, 18 (1882)

[4] Oudemans : Ann Chem (Liebig), **209**, 38 (1881)

[5] Tykociner Rec trav. Chim. Pays-Bas., **1**, 144 (1882).

[6] Oudemans *Ibid.*, **4**, 166 (1885).

In investigations on the effect of concentration on the rotation of salts of malic and camphoric acids it was shown further that their molecular relations, which are very different in strong solutions, become nearly the same for the salts of the same acid as the dilution increases. Thus, the following molecular rotations, $[M]^{20}_{D}$, are calculated from the interpolation formulas found by Schneider[1] for a number of alkali malates, the water present amounting to about 40 to 90 per cent:

		Water in 100 parts by weight of solution					
	Mol wt	40	50	60	70	80	90
Malic acid $C_4H_6O_5$	134	+3.10°	+1.89°	+0.68°	−0.59°	−1.71°	−2.91°
Acid salts							
Li $C_4H_5O_5$......	140	−3.82	−5.44	−8.60	−10.16	−11.28	−11.77
(NH_4) “	151	−7.72	−8.15	−8.58	−9.01	−9.45	−9.89
Na “	156	+0.08	−2.65	−5.04	−7.05	−8.72	−10.02
K “	172	−4.92	−5.87	−6.83	−7.77	−8.74	−9.68
Neutral salts							
Li_2 $C_4H_4O_5$.	146	+5.90	−0.26	−5.62	−10.09	−13.77	−16.54
$(NH_4)_2$ “ .	168	−7.29	−8.13	−9.17	−10.35	−11.74	−13.27
Na_2 “ ...	178	+5.73	+1.16	−3.17	−7.16	−10.93	−14.31
K_2 “	210	−5.15	−7.43	−9.47	−11.32	−12.87	−14.26

As plainly evident, the rotations of these salts in concentrated solutions are very different among themselves, and even differ in sign, but with increasing dilution they become more and more uniform. Further, it is seen that the free malic acid shows a molecular rotation very different from that of the malates.

An explanation of these phenomena was first given by Hädrich[2] in 1893, and based on the theory of electrolytic dissociation which meanwhile had been proposed by Arrhenius. Hädrich makes it clear, that the closely agreeing rotations which the different salts of an active acid or base exhibit in equimolecular solutions, have a meaning as soon as it is assumed that these bodies, as electrolytes, become largely dissociated into their ions on sufficient dilution, because then from each one the same amount of active acid or base ions would be formed. In accordance with this view he gave to the law expressed by Oudemans, this extension:

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[1] Schneider: Ann Chem. (Liebig), 207, 257.

[2] Hädrich · Ztschr phys Chem., 12, 476.

The rotating power, not only of salts, but of electrolytes in general, is, in approximately completely dissociated solutions, independent of the inactive ion.

A confirmation of this law was given by Hädrich by showing that when an alkaloid is neutralized by different acids, and the solutions then are treated with increasing amounts of water, (1), the molecular rotations become constant for each salt from a certain concentration on, and, (2), that the constant values for the molecular rotations of the different salts agree also among themselves, as shown by the observations already given. In the following table, giving some of these experiments, the numbers show the molecular rotations of the salts[1] and under *V* is given the volume of water in liters, in which one gram equivalent of the salt is dissolved:

	Quinidine			Morphine		
V	Hydrochloride	Nitrate	Sulphate	Hydrochloride.	Nitrate	Sulphate
10	...	...	...	− 359°	− 361°	− 357°
20	+ 703°	+ 703°	+ 702°	364	364	364
30	712	710	710	365	365	365
40	717	717	717	371	368	368
60	719	723	719	370	370	365
80	726	726	726	374	369	374
120	723	723	723	..	...	...
160	726	726	726	...	...	...

V	Brucine		Strychnine			
	Hydrochloride	Nitrate	Hydrochloride	Nitrate	Sulphate	Amygdalate
10	− 156°	− 156°	...	...	...	...
20	141	141	− 113°	− 114°	− 113°	− 113°
30	138	138	114	114	114	114
40	136	136	113	113	113	113

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[1] Instead of giving the molecular rotations, the observed angles for a given tul length could have been given, as the solutions contain in equal volumes, the san amount of the corresponding alkaloid.

The quinidine and morphine salts show at first an increase in rotation with increasing dilution and constant values are reached when the dilution of the first, *V*, is brought [illegible] liters and of the second to 40 liters. The alkaloid ion possesses, therefore, in both cases a greater rotating power than the undissociated salt molecule. With brucine the opposite is the case; and the strychnine salts appear to be already dissociated in N/20 solution.

The agreement in molecular rotation in dilute aqueous solutions has been observed in many other salts containing active bases or acids, although sometimes with considerable variations, the cause of which is found partly in insufficient dilution, and partly in the unequal degrees of dissociation for the different salts. Further, it must be remembered that in dilute solutions, as the observed angles are very small, experimental errors exert a great influence on the final result. Observations have been made on the following substances· Alkali salts of malic acid (Schneider),[1] tartrates of different metals (von Sonnenthal,[2] Pribram),[3] tartrates of substituted amines (Kannonikoff),[4] alkali salts of methyl and ethyl tartaric acid (Fayollat),[5] salts of active glyceric acid (Frankland and Appleyard),[6][7] salts of quinic acid (Cerkez),[8] alkali salts of active valeric acid and compounds of valeric acid with inactive organic bases in alcoholic solutions (Guye and Rossi),[9] salts of amyl sulphuric acid and salts of active di-isoamyl amine (Carrari and Gennari),[10] conine hydrochloride and hydrobromide (Zecchini),[11] nicotine salts (Schwebel,[12] Carrari),[13] cinchonidine salts (Schuster),[1] salts of *d*- and *l*-menthylamine (Binz).[2]

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[1] Schneider Ann Chem (Liebig), **207**, 257

[2] v Sonnenthal Ztschr. phys Chem., **9**, 656

[3] Pribram Wien Monatsh , **14**, 742

[4] Kannonikoff. J russ phys-chem Ges., **22**, 36

[5] Fayollat Compt rend , **117**, 632.

[6] Frankland and Appleyard: J Chem Soc , **63**, 296

[7] Frankland and Appleyard, J Chem Soc., **63**, 311, observed, especially with the magnesium, zinc and cadmium salts of active glyceric acid, variations in the molecular rotation from that found with the alkali salts, and in consequence of this were inclined to question the universality of the Oudemans rule. But they used 10 per cent solutions, in which the dissociation was incomplete, and which likewise for the different salts, especially those of the dyad metals, might be very unequal in extent

[8] Cerkez: Compt. rend , **117**, 174

[9] Guye and Rossi: Bull. Soc Chim., [3], **13**, 465

[10] Carrara and Gennari Ztschr phys Chem , **17**, 561.

[11] Zecchini: Ztschr. phys, Chem , **16**, 246.

[12] Schwebel: Ber. d chem. Ges., **15**, 2850.

[13] Carrara: Ztschr. phys. Chem , **14**, 562, **16**, 244.

Of observations of this character, those which Walden[3] made on *α*-bromcamphorsulphonic acid and its salts, may be given here because there was found at the same time the extent of dissociation by means of determination of the electrical conductivity The solutions contained equivalent amounts, and *c* indicates the number of grams in 100 cc. *α* is the angle of rotation found for a column 4 dm. in length at a temperature of 20.5°.[4]

	c	α_D	$[\alpha]_D$	$[M]_D$	Dissociation in per cent
Free-α-bromcamphor-	14.952	+ 55.20°	+ 92.3°	+ 287°	68.5
sulphonic acid.	1.0366	3.64	87.7	273	92.7
$C_{10}H_{11}BrO.SO_3H$	0.5183	1.795	86.6	269	94.4
$M = 311.$	0.2592	0.901	86.9	270	95.5
Potassium salt.	1.1633	3.644	78.3	273	83.6
$C_{10}H_{11}BrO.SO_3K$	0.5817	1.793	77.1	269	87.2
$M = 349.$	0.2908	0.898	77.2	269	90.3
Thallium salt	1.7134	3.633	53.1	273	83.9
$C_{10}H_{14}BrO.SO_3Tl$	0.8567	1.817	52.9	272	87.3
$M = 514.$	0.4283	0.903	52.7	271	90.5
Zinc salt.	1.1417	3.620	79.3	272	71.5
$\frac{1}{2}[(C_{10}H_{14}BrO.SO_3)_2.Zn]$	0.5709	1.795	78.6	269	77.2
$M = 342.5.$	0.2854	0.900	78.8	270	81.8
Barium salt.	1.2617	3.630	71.9	272	69.8
$\frac{1}{2}[(C_{10}H_{14}BrO\ SO_3)_2.Ba)$	0.6309	1.807	71.6	271	74.8
$M = 378.5$	0.3154	0.895	70.9	269	79.4

As can be seen, the molecular rotations of all these bodies in dilute solution approach rapidly the constant value of 269 to 270, even the salts of dyad metals, although these are less dissociated than the alkali metal salts or the free acid. In general, a relatively small change in the molecular rotations is observed, corresponding to the increasing degree of dissociation.

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[1] Schuster: Wien Monatsh., 14, 573.

[2] Binz: Ztschr. phys. Chem., 12, 734.

[3] Walden: Ztschr. phys. Chem., 15, 196. Kipping and Pope, also, (J. Chem. Soc., 63, 548) have investigated some salts of the acid.

[4] The original paper contains observations for the sodium and glucinum salts

Free acids which behave as good electrolytes, must show, in sufficiently dilute solution, the same molecular rotation as the neutral salts, since the concentration of the active ions is finally the same. This is illustrated with α-bromcamphorsulphonic acid described above If, on the other hand, the acid is a poor electrolyte and at the same time is dibasic, as tartaric acid or malic acid, then in consequence of the lower degree of dissociation and also of the formation of different active ions (for example, $C_4H_5O_5$ and $C_4H_4O_5$ from $C_4H_6O_5$) the observed molecular rotation will depart widely from that of the neutral salts.[1] The acid salts also may not agree with these, because here different conditions of dissociation obtain. These differences are shown in the following table which embraces observations of Schneider[2] on malic acid and malates in 5 per cent. solutions, and of Landolt[3] on tartaric acid and tartrates:

	Malic acid	$[M]_D$	Tartaric acid	$[M]_D$
Free acids.	$C_4H_6O_5$	− 3.2°	$C_4H_6O_6$	+ 21.1°
Acid salts.	Li $C_4H_5O_5$	− 11.9	Li $C_4H_5O_6$	+ 42.8
	Na "	10.5	Na "	41.2
	K "	10.2	K "	42.5
	NH_4 "	10.1	NH_4 "	42.8
Neutral salts	$Li_2C_4H_4O_5$	− 17.7	$Li_2C_4H_4O_6$	+ 58.1
	Na_2 "	16.0	Na_2 "	59.9
	K_2 "	14.8	K_2 "	64.4
	$(NH_4)_2$"	14.1	$(NH_4)_2$"	63.0

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[1] From the measurements of Ostwald (Ztschr phys Chem , 3, 371) on the electrical conductivity of tartaric acid, it follows that this acid in a concentration of 0.3 gram per liter is only about one-half dissociated, while the extent of dissociation for the neutral tartrates can be taken as above 95 per cent.

[2] Schneider· Ann Chem. (Liebig), 207, 257. The numbers given are calculated from the interpolation formula given for $q = 95$

[3] Landolt: Ber. d. chem. Ges., 16, 1076 The concentrations employed were equivalent to 7.69 grams of tartaric acid in 100 cc for the neutral tartrates. Weaker solutions were used for the acid salts.

The acid salts in respect to their rotation stand between the free acids and the neutral salts. From them, for example from the acid malates, at first, in the main, the ion C_4H_5O separates, which with greater dilution passes into $C_4H_4O_5$ Finally the same molecular rotation should be expected as with the neutral salts but sufficient observations are lacking to show this.[1]

With the salts of very weak bases and acids besides the electrolytic, hydrolytic dissociation may also take place, by which the number of atomic aggregations in the liquid is stil further increased Such complicated changes appear to take place with the di-hydrochlorides of the cinchona alkaloids inasmuch as these do not, like the monohydrochlorides, give a constant end value for the molecular rotation by increasing dilution. The following numbers for $[M]_D$ were found by Hädrich,[2] in which 1 gram-molecule of substance was contained in V liters:

V	10	20	40	80	160	320
Cinchonidine-						
dihydrochloride. ..	— 525°	— 521°	— 516°	— 504°	— 465°	.
monohydrochloride	— 356	— 381	— 400	— 402	. .	.
Quinidine-						
dihydrochloride ...	+ 1011	+ 1028	— 1043	+ 1049	+ 1123	+ 1225
monohydrochloride	..	+ 703	+ 717	+ 726	+ 726	..

The great differences between the mono- and dihydrochlorides are without doubt caused not only by differences in the nature of the electrolytic dissociation but also, especially with quinidine, by the existence of other kinds of dissociation.

If the degree of dissociation of an active body be diminished by adding to the solution other substances which also behave as electrolytes, a change in the rotating power follows. Acids must produce such an action and in fact it has been found tha the specific rotation of tartaric acid experiences a decrease when the aqueous solution is treated with hydrochloric, nitric sulphuric, or acetic acid. Equivalent amounts of these acids exert influences in different degrees (Landolt).[1] Oudemans[2] observed the same phenomenon on treating di-acid alkaloids with 1, 2, 3, ..., molecules of different acids. At first an increase in the specific rotation follows and continues to a maximum, which appears when somewhat more acid is present than is required for formation of the neutral salt, and then a continuous decrease takes place. Of numerous observations the following may be given:

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[1] The interpolation formulas of Schneider gave for $q = 100$ very great difference between the acid and neutral malates

[2] Hadrich Ztschr phys Chem., 12, 491.

Cinchonine.—In 100 cc of solution 5 mg. molecules of alkaloid + *n* mg. molecules of acid. The maximum values are shown by *·

Mol acid to 1 mol base	Hydrochloric acid	Nitric acid	Formic acid
1	$[\alpha]^{16}_{D} = +201.0°$	+ 191.7°	....
2	254.1	253.4	242.2°
2½	259.0*	257.3	243.9
3	258.7	257.8*	245.6
4	257.7	254.6	250.7
6	253.3	252.1	256.6
10	252.1	251.8	257.8
20	246.0	.	258.9*
45	..	.	257.9
92	..	..	254.0

The increase in the rotation at the beginning may possibly be explained by the assumption of hydrolytic dissociation on addition of small amounts of acid. The behavior of the acids depending on their different degrees of affinity is also evident, inasmuch as to reach the maximum rotation unequal amounts, of hydrochloric acid, 2½ mols, of formic acid, on the other hand, 20 mols., are required

Alkalies act in the same manner as acids From observations of Th. Thomsen[3] it appears that the specific rotation of neutral sodium tartrate undergoes a progressive decrease on addition of increasing amounts of sodium hydroxide, while by addition of water, on the other hand, it increases.

In the same way the changes in specific rotation which

[1] Landolt· Ber. d chem Ges, 13, 2331

[2] Oudemans: Rec. trav. Chim. Pays-Bas, 1, 28

[3] Th Thomsen· J. prakt. Chem. [2], 35, 145; also Aignan. Compt. rend, 112, 1009

follow by addition of salts (§ 70) depend largely on alteration in electrolytic dissociation.

If, finally, active electrolytes are dissolved in liquids whicl possess a smaller dissociating power than water, the specifi rotation in comparison with that in the latter will assume new value, which may be larger or smaller according as th active ion possesses a greater or less rotating power than th undissociated molecule. The same phenomenon must b observed when such a liquid, for example alcohol or acetone is added to an aqueous solution of the body. Among th many observations on this point, the following by Walde may be quoted in which the extent of dissociation has bee calculated from the electric conductivity:

Substance.	Solvent	c	$[M]_D^{25}$	Dissociation Per cent
α-Brom-camphor sulphonic acid	Water................	1.0366	+ 273°	92.7
	7 parts water + 93 parts acetone ...	1.0366	343	5.9
	Water................	0.5183	269	94.4
	3.5 parts water + 96.5 parts acetone .	0.5183	326	4.1
α-Brom-camphor barium sulphonate	Water................	1.2617	272	69.8
	7 parts water + 93 parts acetone ...	1.2617	328	8.1
	Water................	0.6309	271	74.8
	3.5 parts water + 96.5 parts acetone .	0.6309	301	5.0

Oudemans[2] found that some of the salts of the cinchor alkaloids rotate in alcoholic solution more strongly than aqueous, others less strongly.

In general many of the variations shown in the specific rot tion of bodies dissolved in different solvents depend on diffe ences in the extent of electrolytic dissociation, provided dilu solutions are considered.

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[1] Walden: Ztschr. phys. Chem., 15, 205.

[2] Oudemans: Rec. trav. Chim. Pays-Bas, 1, 18.

Dissociation of Salts with Active Anion and Kation.—For such bodies the experiments of Walden[1] have shown, as was to be expected, that the rotations in dilute solutions are equal to the sum of the rotations for the ions. For α-bromcamphorsulphonate of morphine, $C_{10}H_{14}BrO.HSO_3.C_{17}H_{19}NO_3$, dissolved in water, he found:

$$c = 1.9867 \qquad [M]_D = -100^\circ$$
$$c = 0.9933 \qquad [M]_D = -101^\circ$$

For the morphine ion we have, according to the experiments of Hädrich, cited above, the values -365 to 374, in the mean -371 for $[M]_D$. For the ion of bromcamphor sulphonic acid we have $[M]_D = +269$ to $+273$, in the mean $+271$. Hence as molecular rotation of the dissociated salt we must have

$$[M]_D = -371 + 271 = -100^\circ,$$

which agrees with the above observation

This behavior is shown also with quinidine α-bromcamphor sulphonate, where both ions are right rotating.

Behavior of Boryl, Arsenyl and Antimonyl Tartrates.—These compounds which are formed by heating acid tartrates with boric acid, arsenious oxide and antimonious oxide show marked deviations in their rotating power from the ordinary neutral tartrates. With the latter the rotation increases with increasing dilution and reaches a constant value which corresponds to the completely separated ion, $C_4H_4O_6$. Thus from the formula of Th Thomsen[2] for *d*-sodium tartrate,

$$[M]_D^{20} = 60.56 - 0.04647\,p - 0.002216\,p^2,$$

the following numbers may be calculated for solutions which contain V liters of water for 1 gram-mol. of salt (or in 100 parts of solution p grams of salt) These values for $[M]_D$ change but little.

V	1	2	4	8	16	32
$p =$	0.1625	0.0884	0.0462	0.0238	0.0120	0.0060
$[M]_D =$	+ 59.22	59.98	60.30	60.45	60.50	60.53

The same end value, as remarked before, is found with the other neutral tartrates.

On the other hand Hädrich found for certain alkali boryl tartrates the following molecular rotations, when the same dilutions were employed (1 gram-mol. of salt in V liters).[1]

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[1] Walden: Ztschr. phys. Chem., 15, 206.

[2] Thomsen: Jour prakt. Chem. [2], 34, 80

V.	$K(BO)C_4H_4O_6$.	$Na(BO)C_4H_4O_6$.	$NH_4(BO)C_4H_4O_6$.
1	+ 143°	+ 152°	+ 148°
2	134	138	136
4	121	122	121
8	106	107	107
16	88	89	89
32	74	74	74

We have here to begin with a much larger molecular rotation than with the simple tartrates, and this is explained by the circumstance that the separated ion is not $C_4H_4O_6$, but $C_4H_4O_6.BO$. Secondly, the rotation decreases rapidly with increasing dilution and for $V = 16$ is not yet approaching constancy. As appears from the investigations of Magnanini[2] on the conductivity of solutions of boro-tartaric acid this may be referred to gradual hydrolysis taking place at the same time which brings about a decomposition of the complex ion, $C_4H_4O_6.BO$. Finally the ion $C_4H_4O_6$, with $[M]_D = 60.5$, must be present.

The arsenyl tartrates act in the same way. Hädrich found for $[M]_D$:

V	$Na(AsO)C_4H_4O_6$.	$NH_4(AsO)C_4H_4O_6$
2	+ 224°	+ 230°
4	185	186
8	131	132
16	79	80
32	63	63

With these compounds in the most dilute solution the rotation of the tartaric acid ion (58 to 63 as already given) has been reached.

Other phenomena are shown by potassium antimonyl tartrate (tartar emetic). Here we have very strong rotation which scarcely decreases by dilution. For the formula $KSbOC_4H_4O_6$ Hädrich[3] found these numbers:

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[1] Hädrich: Ztschr. phys. Chem., 12, 494.

[2] Magnanini: *Ibid.*, 6, 67.

[3] Hädrich: *loc. cit.*

V	4	8	16	32	64
α_D for $l = 2.35$ dm.	+ 13.70	6.85	3.42	1.70	0.85°
$[M]_D$	+ 548	548	546	544	544
Mol. conductivity, μ	...	70.58	79.45	87 63	94.20

Some hydrolysis takes place here as shown by Hädrich from the manner of change in the conductivity, but only to a slight extent. An explanation of the slight change in the molecular rotations is still lacking

62. b. **Formation or Decomposition of Molecular Aggregations of Simple Structure.**—As is well known molecular weight determinations by the freezing- or boiling-point method have shown that many substances, liquid as well as solid, when dissolved in certain liquids appear as single molecules, while in others they exist as double molecules (for example, acetic acid in ether $C_2H_4O_2$, in benzene = $(C_2H_4O_2)_2$, etc.). Experiments have accordingly been made to determine whether the influence which several solvents, or their concentrations, exert on the specific rotations of many substances corresponds to a change in the molecular weight of the latter. On this subject we have, mainly, the following investigations

Freundler[1] dissolved a number of tetra-substituted tartaric acid esters, the rotations of which in pure condition were known, in different liquids ($c = 5$ to 6) and determined the specific rotation and the molecular weight He believes the following laws obtain for these bodies

1. In solvents which change the rotation of the esters but little or not at all, the latter show the normal molecular weight. For example:

Solvent.	Active substance	Molecular weight		Spec rot $[\alpha]_D$.	
		From the formula	Observation	In solution	Without solvent.
Ethylene bromide	Propyl dipropionyl tartrate	346	342	+ 5 4°	+ 5 5°
	" dibutyryl "	374	363	+ 5 5	+ 5.2
	" divaleryl "	402	389	+ 3.6	+ 3.6
	" dicaproyl "	430	424	+ 2.4	+ 2.2
	Methyl divaleryl "	346	348	— 15.6	— 15.9
Benzene	Isobutylamyl oxide	144	141	+ 1.4	+ 1.3

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[1] Freundler: Ann. chim. phys, [7], 4, 256 (1895)

2. In solvents which bring about a marked change in the original specific rotation of the esters, anomalous numbers are found in the cryoscopic molecular weight determinations. For example:

Solvent.	Active substance	Molecular weight		Spec. rot $[\alpha]_D$.	
		From the formula	Observation.	In solution $c = 5$ to 6	Without solvent
Benzene	Propyl diacetyl tartrate	318	277	+ 1.2°	+ 13.4°
"	" dipropionyl "	346	295	− 3.4	+ 5.6
"	" dibutyryl "	374	304	− 1.4	+ 5.2
"	" divaleryl "	402	324	− 2.2	+ 3.3
"	" dicaproyl "	430	345	− 4.3	+ 2.2
Nitrobenzene	Isobutyl diacetyl "	346	318	+ 12.0	+ 17.0
Nitrobenzene	Ethyl dicaproyl "	402	376	− 5.1	− 3.1
Acetic acid	Isobutyl dipropionyl "	374	287	+ 20.2	+ 10.2
Ethylene bromide	Ethyl diphenylacetyl tartrate	442	394	+ 19.2	+ 15.2
Ethylene-bromide	Propyl " " "	470	406	+ 23.3	+ 20.9
Benzene	" " " "	470	413	+ 15.7	+ 20.9
Nitrobenzene	" " " "	470	378	+ 14.6	+ 20.9
Acetic acid	" " " "	470	377	+ 27.2	+ 20.9

In all these cases, the specific rotation of the dissolved substance is markedly different from that of the original solvent-free body, being sometimes higher, sometimes lower, and sometimes showing a change in direction. The molecular weights, as determined, are all below the normal, which probably depends on dissociation of the compounds.

Freundler also found substances whose molecular weights in solution are much larger than the formula weights and which show marked changes in rotating power. The explanation here may be found in polymerization. The following simple esters of *d*-tartaric acid behave in this manner.

Solvent.	Active substance.	Molecular weight		Spec. rotation $[\alpha]_D$	
		From the formula	Observation.	In solution	Without solvent.
Benzene	Methyl tartrate	178	411	— 8 8	+ 2.14
Benzene	Propyl "	234	306	+ 20.1	+ 12.44
Ethyl bromide	" "	234	326	— 0.6	+ 12 44

The rotation and molecular weight of nicotine in different solvents has been investigated by Hein,[1] and with concentrations at which the boiling-point method yields reliable results. It was found that by diminishing the percentage amount of nicotine, p, the specific rotation was also diminished, although with several liquids, as ether, acetone, and benzene, in very small degree, and somewhat more with ethyl and propyl alcohol The molecular weights appear from the observations to undergo a slight decrease with decrease in p, but the values are all very near the normal number. The following are the results obtained

Pure nicotine. $\alpha^{20}_D = - 164.0°$ Molecular weight = 162

Solvent	Decrease in percentage amount of nicotine	Corresponding decrease in specific rotation $[\alpha]^{20}_D$	Molecular weight found
Ethyl alcohol.	From 11 4 to 1.7	From — 141.1° to 139 0°	167 to 164
Propyl alcohol	" 13 4 " 2 0	" — 147 2 " 144 6	156 " 152
Ether	" 19 9 " 4 6	" — 162 3 " 161 8	192 " 177
Acetone	" 12 0 " 2 3	" -- 163 3 " 162 6	188 " 172
Benzene	" 14.4 " 3.5	" — 163.8 " 163 4	175 " 172

Solutions of nicotine in water show, on the other hand, a different behavior. As pointed out in § 56 the specific rotation changes within the limits $[\alpha]^{20}_D = - 76.84$ to 77 59 when the percentage strength sinks from $p = 15.59$ to 1.06, with a minimum at $p = 9$ The molecular weight, found cryoscopically, shows however, according to the observations in § 56, a very strong decrease; it has for $p = 13.74$ the value 275, which gradually sinks to the normal, 162, when p is less than 2 per cent. In this case the great change in molecular weight has no influence on the rotating power of the substance.

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[1] J. Hein Ueber das specif. Drehungsvermögen und das Moleculargewicht des Nicotins in Lösungen, Inaug. Diss., Berlin (1896).

Rotation and molecular weight in solutions of different concentrations have been further investigated by Frankland and Pickard[1] with the following substances

Solvent	Decrease in per centage amount of active substance	Corresponding change in specific rotation, $[\alpha]_D$.	Molecular weight found cryoscopically
d-Dibenzoylglycerate of methyl $[\alpha]_D^{15} = + 26.9$; $M = 328$.			
Benzene	34.1 to 3.0	Inc from + 40.7 to 45.7	Between 299 and 322
Nitrobenzene	28.1 “ 2.4	Dec. “ + 22.0 “ 19.8	“ 305 “ 341
Ethylene-bromide	22.3 “ 3.3	“ “ + 21.7 “ 19.2	“ 322 “ 359
Acetic acid	18.6 “ 1.7	Inc “ + 32.4 “ 34.3	“ 305 “ 341
l-Diacetylglycerate of ethyl $[\alpha]_D^{15} = - 16.31$; $M = 218$.			
Benzene	29.8 to 5.3	Inc. from — 14.8 to 17.2	Dec from 216 to 209
Acetic acid	25.0 “ 3.4	“ “ — 19.4 “ 28.7	“ “ 194 “ 136

With the first ester, no definite change in the molecular weight, corresponding to increase or decrease in the specific rotation with diminished concentration, is noticed; for the molecular weight, irregularly varying numbers were found, which are not very far from the normal formula weight.

The diacetylglycerate of ethyl dissolved in benzene shows an increase in rotation, but a decrease in the corresponding nearly normal molecular weight. In acetic acid, the rotation increases likewise and the molecular weight decreases, but the latter shows values which are much smaller than the normal, so that dissociation appears to have taken place here.

With the ethyl ester of *l*-mandelic acid, the following values were found by Walden[2] for the specific rotation and molecular weight, the latter being determined by elevation of the boiling-point:

[1] P Frankland and Pickard J Chem Soc, 69, 123

[2] Walden Ztschr phys Chem, 17, 705

Pure ester (superfused) $[\alpha]_D = -123.1^\circ$; $M = 180$.

Solvent.	c	$[\alpha]_D$	Molecular weight found
Acetone	5.81	− 90.6°	175.4 (4.21 subst. in 100 pts. solution)
"	1.16	− 87.1	
Carbon disulphide	5.00	− 180.0	189.6 (3.64 " " ")
" "	2.50	− 180.0	

The original specific rotation of the ester experiences, therefore, in acetone a marked decrease, but in disulphide of carbon, on the other hand, an increase, while the molecular weight is normal in both solutions.

Finally, α-mononitrocamphor dissolved in carbon disulphide shows a strongly decreasing rotation with increase in concentration, but in alcohol only a slight change. In both solvents the substance possesses the normal molecular weight (Pescetta).[1]

According to the above observations the following phenomena, in general, have been noticed:

1. A change in the rotation, with the molecular weight remaining normal (ethyl mandelate, α-mononitrocamphor, nicotine in ethyl and propyl alcohol)

2. A change in the molecular weight while the rotation remains constant (nicotine in water). In these two cases there can, naturally, be no relation between the constants

3. Simultaneous changes in rotation and molecular weight. If here the molecular weight in solution is much greater than the normal, the cause of the modified rotation is probably found in a polymerization of the molecule (simple tartrate esters) If the molecular weight is found to be smaller than the normal, the change in rotation is probably due to beginning dissociation (diacetyl glycerate of ethyl in acetic acid).

Whether or not the variations from the original specific rotation which were found in the tetra-substituted esters of tartaric acid, investigated by Freundler, when they were dissolved in different solvents, have any connection with the decrease in molecular weight observed at the same time, can not be shown with certainty.

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[1] Pescetta: Gazz. chim. ital., 25, II, 418.

63. c. Presence of Complex Polymerized Molecules (Crystal Molecules) in the Solution.—While it is not clear how by association of two or only a few molecules the original rotation should be altered, some action should follow, on the other hand, when a large number of active molecules unite to produce a crystal structure, which in turn possesses asymmetric form. It has already been shown, in § 7, that those bodies which are active in dissolved and in crystalline condition possess, in the latter form, a rotating power which is due to the combined activity of the single molecules and the crystal molecules. If the assumption may be made that in concentrated solutions, at least, of solid active substances, such complex aggregations are present, which by continued dilution gradually break down into normal molecules, then the corresponding changes in the rotation may be explained.

The possibility of the occurrence of such crystal molecules in solutions has been frequently affirmed by Groth,[1] Fock,[2] Bell,[3] Wyrouboff[4] and others, but experimental proof is thus far wholly lacking. It is, however, possible that the following phenomena observed in aqueous solutions of malic and tartaric acids may be ascribed to this cause.

Ordinary malic acid exhibits left rotation in dilute aqueous solutions, and this grows less with increasing concentration, passes through a point of inactivity, and finally turns to increasing right rotation (§ 57). The same phenomenon is noticed on lowering the temperature (§ 60). With *d*-tartaric acid, on the other hand, the rotation changes from right to left gradually as the concentration becomes very great (§ 46). For each spectrum color the point of inactivity appears at a certain and distinct concentration (§ 46).

These marked variations in the rotation *can not* be explained, as Nasini and Gennari[5] especially have pointed out, by (1) electrolytic dissociation, because this with malic acid and tartaric acid is noticeable only in very dilute solutions, where an accurate observation of the rotation could no longer be made;

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[1] Groth: "Physikal. Krystallog.," III ed. (1895), p 268.

[2] Fock: "Einleitung in die chemische Krystallographie" (1888), p 19

[3] Louis Bell: Silliman's Jour. [3], 7, 120.

[4] Wyrouboff: Compt. rend., 115, 832; Bull. Soc. Chim., [3], 9, 214

[5] Nasini and Gennari: Ztschr. phys. Chem., 19, 113

(2) by simple polymerization, as cryoscopic observations with malic acid in concentrations 9 and 24.5 have shown the normal molecular weight; (3) by formation of hydrates of variable composition; for the reasons given in § 64 these are in general not possible.

The phenomenon may be understood, however, if we assume that the left-rotating single molecules of malic acid with increasing concentration gradually combine to form right-rotating aggregations, and the right-rotating tartaric acid molecules to form left-rotating groups. Accordingly, finally, in anhydrous condition, *l*-malic acid should exhibit right rotation and *d*-tartaric acid left rotation. With the first acid this has not been shown experimentally,[1] but in the case of tartaric acid it has been, as already mentioned in § 46 That this condition can actually obtain when solid crystalline particles separate is shown in the case of rubidium tartrate, which, as explained in § 7, possesses right rotation in solution, but left rotation as salt.

The assumption that in solutions of malic and tartaric acids, single molecules and molecular aggregations occur at the same time, and possess opposite rotations, would explain (1) The anomalous rotation dispersion of the two substances (§ 46); (2) the parallel change in rotation with increasing dilution or elevation of temperatures (§ 60), as both causes would lead to a breaking down of molecular aggregates, (3) the phenomenon referred to in §59 in which solutions of *d*-tartaric acid in mixtures of alcohol and benzene or other hydrocarbons exhibit left rotation, inasmuch as these liquids, as is well known, have the power of favoring the formation of molecular combinations

A proof of aggregations by cryoscopic methods is not possible, as these do not exist in dilute solutions In such solutions, as shown in § 20, tartaric acid has the normal molecular weight. The further changes observed in the rotation of tartaric acid, with great dilution (§ 55), find their explanation in the now possible electrolytic dissociation.

As may be finally remarked, phenomena different from those referred to above had already led to the view that molecular combinations exist in concentrated solutions which break down with increasing dilution Hittorf explains in this way the abnormal behavior of cadmium salts on electrolysis.[1]

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[1] This has since been shown by Walden See Part VI, Constants of Rotation Tr

64. **d. Combinations of the Active Body with the Solvent. Hydrates.**—Biot[2] attempted to explain the changes in the specific rotation of tartaric acid on increasing dilution on the assumption of the formation of hydrates containing more and more water. But thus far, it has not been found possible with this substance or with others to positively prove the existence of such compounds, as the methods based on observations of osmotic pressure furnish here no information. As Nernst[3] has shown, a progressive formation or decomposition of hydrates with increasing dilution is in general not possible, and for the following reasons If a molecule, A, with n molecules of another substances B (water) enters into the reversible reaction,

$$A + n\,B = A\,B_n,$$

and the corresponding concentrations are,

$$c_1 \quad c_2 \quad c,$$

then must, by the Guldberg-Waage law,

$$Kc = c_1\,c_2^{\ n}.$$

If the molecule species, B, represents the solvent, present in excess, then its concentration, c_2, in comparison with c_1 and c, is very large, and it will be but little changed in the reaction, whatever direction this takes. Consequently c_2 may be combined with the constant K and we have :

$$\frac{c}{c_1} = \text{const.};$$

that is, *for all concentrations, the relation of the hydrated to the non-hydrated molecules must remain the same.* This law would naturally no longer obtain if the substance on solution should form several kinds of groups, A, by polymerization or chemical decomposition.

Hydrates of definite composition are without doubt formed by the solution of certain active bodies in water. This is indicated, for example, by the strong liberation of heat in the case of *nicotine* (15° for 24 grams of nicotine and 6 grams of water); also by the phenomenon that strong solutions separate, on heating, into the oily base and water. Further, as follows from the observations cited in § 52, the density of the solutions increases with increasing addition of water, reaches a maximum with the proportions 65.9 nicotine to 34.1 water (corresponding to $C_{10}H_{14}N_2.5H_2O$) and then rapidly decreases. This peculiarity in the variations in the specific gravity is not shown however, in the continuous decrease exhibited by the specific rotation, and it may therefore be questioned if the latter is influenced by the nicotine hydrate.

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[1] See H. Jahn "Grundriss der Electrochemie," Vienna, 1895, pp. 49 and 57.
[2] Biot, Mém. de l'Institut, T 15 (1838)
[3] Nernst Ztschr. phys Chem, 11, 345, "Theoretische Chemie," p. 370.

The changes in the rotation of aqueous solutions of malic acid, referred to in § 57, have been accounted for by Bremer[1] on the assumption that the acid itself possesses right-hand rotation while the hydrates,

$$\begin{gathered}COOH{-}CH.OH{-}CH_2{-}C(OH)_3,\\ C(OH)_3{-}CH.OH{-}CH_2{-}C(OH)_3,\end{gathered}$$

show left-hand rotation.

Further, the phenomenon that rhamnose hydrate, $C_6H_{12}O_5, H_2O$, dissolved in water on the one hand, and in certain alcohols on the other, exhibits opposite rotation directions, has been explained by Rayman[2] on the hypothesis that the solution contains a hydrate, $C_5H_{11}O_4.CH(OH)_2$, in the one case and in the other, alcoholates, $C_5H_{11}O_4$ *$CH(OH)(OR)$, in which a new asymmetric carbon atom appears The observed specific rotations referred to $C_6H_{12}O_5$ are the following:

Water	p 5 to 40	$[\alpha]_D = +$ 9 2 to 9 4[3]
Methyl alcohol .	$p = 19$	$[\alpha]_D = -$ 10 59[4]
Ethyl alcohol ..	$p =$ 6 4; 9.3	$[\alpha]_D = -$ 10 65,[4] 10 0[5]
Isobutyl alcohol..	$p =$ 7 3	$[\alpha]_D = -$ 7.3[4]
Amyl alcohol.. .		left-rotating[4]
Isopropyl alcohol.		$[\alpha]_D = +$ 8 67[6]

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[1] Bremer Rec trav. Chim. Pays-Bas., 3, 162, 336.

[2] Rayman Ber d. chem. Ges., 21, 2050

[3] Rayman and Kruis: Bull. Soc. Chim. (2), 48, 632; Schnelle and Tollens Ann Chem (Liebig), 271, 62; Jacobi: *Ibid.*, 272, 175. The solution of the hydrate in water exhibits at first left rotation, but after a time the constant right rotation appears

[4] Rayman: *loc. cit*

[5] Jacobi· *loc. cit.*

[6] Parizek and Sulc: Ber. d. chem. Ges., 26, 1411.

Of the left-rotating alcoholic rhamnosides Rayman was a to prepare the amyl compound in solid condition. The ri rotation of the solution in isopropyl alcohol is explained Parizek and Sulc,[1] who state that in this case an alcoholat not formed. According to Fisher the alcohol glucosides easily formed in presence of hydrochloric acid [2]

If an active body forms a true chemical combination w the solvent, the resulting specific rotation would naturally different from that found with an inert solvent. This wo be the case, for example, with solutions of borneol in chl or bromal. The existence of such compounds in solutio frequently assumed, for example, of turpentine oil with car disulphide,[3] propyl tartrate with benzene,[4] alkaloids w alcohol and benzene,[5] but that they are formed has not b definitely proved.

65. e. **Hydrolysis.**—This phenomenon occurring in salts weak acids or bases appears to influence the rotation in sc instances, as already pointed out in § 61, but numerical d are still lacking. The effect is probably slight, because, a well known, with most salts but a small portion suffers hyd lytic dissociation (Shields),[6] (Bredig) [7]

66. f. **Small Variations in the Atomic Equilibrium of the Ac Molecule.**—The alteration in specific rotation shown by nea all bodies in presence of a solvent cannot be explained in ma cases, by any of the causes so far discussed. Here, example, belongs the increase in the specific rotation of ca sugar by increasing dilution with water, where between limits $q = 35$ to 95 $[\alpha]_D$ increases from 65.6° to 66.6° (§5 further, the increase in specific rotation of *l*-turpentine $[\alpha]_D = -37$, by addition of alcohol, benzene or acetic ac which liquids finally yield a maximum value of $[\alpha]_D = -38.$ $-39.8°$, and $-40.7°$ (§52) Although in these cases, as many others, the increase or decrease in the rotating powe but small, it may still be followed with certainty.

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[1] Parizek and Sulc *loc cit.*, Sulc. Ber d chem Ges., **27**, 594.
[2] Fisher Ber d chem Ges, **26**, 2400
[3] Aignan. Pouv Rot, Thesis, 1893, p 24
[4] Freundler Bull Soc Chim, [3], **9**, 683
[5] Wyrouboff Jour de Phys [3], **2**, 180; Ann. chim. phys. [7], **1**, 1.
[6] Shields Ztschr phys Chem, **12**, 167.
[7] Bredig *Ibid*, **13**, 322

Phenomena of this order, as already remarked in the first edition of this work, may possibly be accounted for by the hypothesis, that when between the molecules of a certain substance (turpentine) other molecules (alcohol) enter, certain modifications in the structure of the first result and of such a nature that in each molecule, the relative positions of the atoms, their arrangement in space and the conditions of their motions are somewhat altered. This will follow in greater degree, the larger the number of added inactive particles Observations of other kinds of phenomena have also led to the same notions of possible slight perturbations in atomic equilibrium, not sufficient, however, to endanger the existence of the molecule [1]

E. Specific Rotation of Complex Systems

67. Solutions of an Active Body in Two Inactive Liquids.—If the change in the specific rotation of the body by each one of the solvents alone is expressed by the constants of the equations·

$$\text{(I)} \qquad \begin{aligned} [\alpha]_1 &= a + b_1 q + c_1 q^2 \\ [\alpha]_2 &= a + b_2 q + c_2 q^2, \end{aligned}$$

in which a is nearly the same, the action of the mixture will be given by

$$\text{(II)} \qquad [\alpha] = a + (b_1 P_1 + b_2 P_2)q + (c_1 P_1 + c_2 P_2)q^2,$$

where 100 parts by weight of the solution of the active substance contain q parts of the inactive liquid mixture, or 1 part by weight of the latter is made up of P_1 and P_2 parts of the components

This formula applies, however, only when the two liquids mix with but slight change in volume or other physical property, as, in the other event, some modification in the behavior of the same with the active body might be expected.

Rimbach[2] investigated the relations obtaining with solutions of camphor in mixtures of acetic ether and benzene He found, as expressing the influence of the liquids separately:

Camphor in acetic ether $[\alpha]^{20}_D = 56.54 - 0.0907\,q + 0.000\,401\,q_2$

" benzene $[\alpha]^{20}_D = 55.99 - 0.1847\,q + 0.000\,269\,q^2$

Then the specific rotations were determined for a number of solutions which are given below in parallel with the values found by formula (II). For this calculation α was taken 56.265.

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[1] See, for example, van 't Hoff · "Etudes de dynamique chimique," 1884, p. 41

[2] Rimbach: Zeit. phys. Chem., 9, 698.

Mixture. q	Acetic ether. P_1	Benzene P_2	$[\alpha]^{20}_D$		Cal.–Obs.
			Observation.	Calculation.	
49.94	0.7509	0.2491	+ 51.76°	51.49°	0.27
64.98	0.7509	0.2491	50.86	50.41	0.45
90.00	0.7509	0.2491	49.63	48.97	0.66
46.21	0.5050	0.4950	50.88	50.66	0.22
64.96	0.5050	0.4950	49.35	48.77	0.58
79.70	0.5050	0.4950	48.06	47.46	0.60
89.49	0.5050	0.4950	47.32	46.67	0.65
40.16	0.2569	0.7431	50.35	50.31	0.04
50.13	0.2569	0.7431	49.14	48.98	0.16
65.18	0.2569	0.7431	47.41	47.09	0.32
80.00	0.2569	0.7431	45.89	45.36	0.53
89.69	0.2569	0.7431	44.86	44.30	0.56

With these mixtures the calculated specific rotation was always found a little less than that found by observation, the difference increasing with the dilution of the mixture.

A second series of investigations made by Rimbach on solutions of right turpentine oil in mixtures of alcohol and glacial acetic acid showed very small differences between observation and calculation, and sometimes positive, sometimes negative

While in the above illustrations, the specific rotation with mixtures has been found to lie between those found with the components, it has been noticed that in some cases the first may be considerably the larger. In this event, a *maximum rotation* is found for some definite mixture of the two liquids. The following are observations in this line :

According to Hesse[1] cinchonidine gives in concentration, $c = 2$:

Dissolved in alcohol of 97 per cent by volume. $[\alpha]_D = -106.9$
" " chloroform.................... " -83.9
" " alcohol-chloroform (1 : 2)....... " -108.9

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[1] Hesse . Ann. Chem. (Liebig), 176, 219.

For anhydrous cinchonidine nitrate and hydrochloride, Oudemans[1] obtained the following numbers

Solvent.		Nitrate, $c = 1.855$	Hydrochloride, $c = 1.722$.
Water	$[\alpha]_D =$	− 99.9	− 99.9
Absolute alcohol	"	− 103.2	− 104.6
80 per cent.[2] alcohol + 20 per cent[2] water	"	− 127.0	− 128.7
89 " " " + 11 " " "	"	− 119.0	− 119.6

According to Oudemans quinidine hydrochloride in concentration $c = 1.89$, for the anhydrous salt, shows :

Dissolved in water	$[\alpha]_D =$	+ 190.8
" " absolute alcohol	"	199.4
Dissolved in alcohol of 90.5 per cent by weight	"	213.0

Hesse[3] has followed the changes in the specific rotation of quinine hydrochloride (with $2H_2O$) with variations in the proportions of water and alcohol used as a solvent, employing always the constant concentration, $c = 2$. From the following data, in which g gives the per cent. by volume of alcohol in the solvent, it appears that for $g = 60$, a maximum of rotation occurs

$g =$	0	20	40	50	60	70	80	85	90	97
$[\alpha]_D =$	− 138.8	166.6	182.8	187.5	187.8	182.3	174.8	168.3	160.8	143.9

Oudemans[4] gives the following observations on the specific rotation of cinchonine in mixtures of chloroform and alcohol

	1	2	3	4	5	6	7	8	9	10	11
Chloroform	100.00	99.66	98.74	94.48	86.95	82.26	65.00	44.29	27.54	17.02	0.00
Alcohol	0	0.34	1.26	5.52	13.05	17.74	35.00	55.71	72.46	82.96	100.00
$[\alpha]_D$	+ 212.0	216.3	226.4	236.6	237.0	234.7	229.5	226.6	227.6	227.8	228.0

A maximum is found here which is shown by graphic interpolation to occur with the mixture containing 10 per cent. of alcohol. It is also observed that in an alcoholic solution of cinchonine, about one-half of the alcohol may be replaced by chloroform without producing any marked change in the specific rotation, while on the other hand, if in a solution of cinchonine in chloroform only 1/300 of the latter is replaced by alcohol, an increase in the specific rotation of 4° follows.

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[1] Oudemans ; Ann. Chem. (Liebig), 182, 49, 50.

[2] By weight.

[3] Hesse · Ann Chem. (Liebig), 176, 210.

[4] Oudemans : *Ibid.*, 166, 71.

68. Mixtures of Two Active Liquid Substances.—If the mixture consists of

p_1 parts by weight of the one body with specific rotation $[\alpha]_1$,
p_2 " " " other " " " " $[\alpha]_2$,
then we have as the specific rotation of the mixture $[\alpha]_m$:

$$[\alpha]_m = \frac{p_1 [\alpha]_1 + p_2 [\alpha]_2}{p_1 + p_2},$$

assuming that each body has no influence on the specific rotation of the other. If, however, some such action takes place the observed specific rotation must depart more or less widely from that calculated.

An investigation of this question was undertaken by Hammerschmidt[1] with the following substances.

Mixtures of Right- and Left-Rotating Turpentine.

Mixture No.	In 100 parts of mixture		Observed rotation of the mixture $[\alpha]_D^{20}$	Calculated specific rotation	Difference Calc.—Obs.
	Right oil.	Left oil			
	100	...	+ 17.39°	...	...
I	79.25	20.75	+ 6.40	+ 6.41°	+ 0.01
II	60.40	39.60	− 3.54	− 3.55	+ 0.01
III	40.82	59.18	− 13.90	− 13.90	+ 0.01
IV	20.83	79.77	− 28.82	− 28.80	− 0.02
	....	100	− 35.50	....	...

From these numbers it is evident that the specific rotations of mixtures of such similar bodies as two turpentine oils correspond exactly to the above mixture formula. It is further found by calculation that a mixture of 67.13 parts by weight of the right-hand oil with 32.87 parts by weight of the left-rotating oil must be inactive optically.

69. Solutions of Two Active Bodies in an Inactive Liquid.—Let the mixture contain in 100 parts by weight

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[1] Hammerschmidt, "Ueber das specifische Drehungsvermögen von Gemengen optisch activer Substanzen" Inaug. Dissert. Rostock 1889.

A_1 per cent. of the first active substance,
A_2 " " " " second " "
F " " " " inactive liquid,

and let the effect of the solvent on the first active body be expressed by

$$\text{(I)} \qquad [\alpha]_1 = a_1 + b_1 p + c_1 p^2,$$

and that of the solvent on the second active body by

$$\text{(II)} \qquad [\alpha]_2 = a_2 + b_2 p + c_2 p^2,$$

in which formulas p gives the percentage amount of active substance in each solution.

Then we substitute:

In equation (I) for p the value $\frac{100 A_1}{A_1 + F}$;
" " (II) " p " " $\frac{100 A_2}{A_2 + F}$

With the specific rotations $[\alpha]_1$ and $[\alpha]_2$ so obtained, there follows for the mixture,

$$[\alpha]_m = \frac{A_1[\alpha]_1 + A_2[\alpha]_2}{A_1 + A_2},$$

but from the observed angle of rotation a_m we have the value,

$$[\alpha]_m = \frac{100\, \alpha_m}{l \,.\, d\, (A_1 + A_2)}.$$

In order to judge of the difference between observation and calculation, it is preferable to compare the observed angles of rotation directly instead of the specific rotations, from which it will be seen whether or not the errors of observation are exceeded. The calculated angle of rotation follows by equating the last two formulas, as:

$$\alpha_m = \frac{A_1[\alpha]_1 + A_2[\alpha]_2}{100}\, l \,.\, d.$$

These deductions may be tested by some experiments which Hammerschmidt[1] carried out with aqueous solutions containing cane-sugar and grape-sugar. The following tables give first, the observed data, and then the calculations, for which the interpolation formulas of Tollens are used in finding the specific rotations of the two sugars:

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[1] Hammerschmidt; *Loc cit.*

Cane-sugar.... $[\alpha]_D = 66.386 + 0.015035\,p - 0.0003986\,p^2$
Grape-sugar .. $[\alpha]_D = 52.500 + 0.018796\,p - 0.0005168\,p^2$

Solu'n No	In 100 parts by weight			Specific gravity of solution d	Observed angle of rotation for $l = 1.9992$dm α_m	Specific rotation, $[\alpha]_m$ Ray D
	Cane-sugar A_1	Grape-sugar A_2	Water F			
1	5.049	19.490	75.461	1.09996	30.14°	55.83°
2	9.814	14.851	75.335	1.10104	31.81	58.56
3	14.655	9.863	75.482	1.10073	33.06	61.28
4	19.517	4.892	75.591	1.10054	34.25	63.78
5	19.558	4.855	75.587	1.10056	34.30	63.85

Solu'n No	Cane-sugar $\frac{100\,A_1}{A_1 + F}$	Grape-sugar $\frac{100\,A_2}{A_2 + F}$	Cane-sugar $[\alpha]_1$ Ray D	Grape-sugar $[\alpha]_2$ Ray D	Calculated angle of rotation α_m Ray D	α_m Calc.-Obs.
1	6.271	20.526	66.464°	53.104°	30.14°	0.00°
2	11.526	16.467	66.506	52.950	31.68	−0.13
3	16.259	11.557	66.525	52.786	32.91	−0.15
4	20.521	6.078	66.527	52.633	34.23	−0.02
5	20.556	6.035	66.527	52.632	34.25	−0.05

From the slight deviation of the calculated angle of rotation from the observed it follows that cane-sugar and grape-sugar do not sensibly affect each other in their rotating power.

An agreement equally close is found with aqueous solutions of mixtures of cane-sugar and raffinose (meletriose). The specific rotation of each, and especially of the latter, is but slightly dependent on the amount of water, and we can take as constants for:

Cane-sugar........ $[\alpha]_D = +\ 66.5$
Raffinose ..... $[\alpha]_D = +\ 104.5$

In such cases we can employ in the above mixture formula the concentrations c_1 and c_2 in place of the weight per cents., A_1 and A_2, that is, we can consider the number of grams of each substance dissolved in 100 cc. of solution, from which,

$$[\alpha]_m = \frac{c_1[\alpha]_1 + c_2[\alpha]_2}{c_1 + c_2} \quad \text{and} \quad \alpha_m = \frac{c_1[\alpha]_1 + c_2[\alpha]_2}{100} \cdot l.$$

Experiments by Creydt[1] have given the following results:

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[1] Zeit. Ver. fur Rubenzucker-Ind., 1887, p. 153

100 cc solution contains		Angle of rotation $[\alpha]_m$ for tube length $l = 2$ dm			Specific rotation, $[\alpha]_m$		
Cane-sugar, c_1	Raffinose, c_2	Observed for D	Calculated	Calc — Obs	Observed for D	Calculated	Calc — Obs.
16 g	4 g	+ 29.61	+ 29.64	+ 0.03	+ 74.02	+ 74.10	+ 0.08
17 "	3 "	28.92	28.88	— 0.04	72.29	72.20	— 0.09
18 "	2 "	28.11	28.12	+ 0.01	70.28	70.30	+ 0.02
19 "	1 "	27.37	27.37	0.00	68.43	68.43	0.00

Somewhat greater differences between observation and calculation were obtained by Hammerschmidt[1] with mixtures of *d*-camphor and *l*-santonin dissolved in chloroform.

70. **Addition of Inactive Bodies to Solutions of Active Substances.**— According to the nature of the two substances mixed, the increase or decrease in the rotating power noted depends on a change in the chemical equilibrium, the degree of dissociation, or on the formation of new compounds Most of the investigations carried out in this field deal with tartaric acid and malic acid, or with different sugars. Among these the following may be considered

A. Tartaric Acid and Malic Acid.

a. Influence of Alkali Salts on the Rotation of Tartrates —A series of investigations carried out by Long[2] relates to potassium sodium tartrate, $KNaC_4H_4O_6.4H_2O$, the specific rotation of which changes but little within the limits, $c = 5$ to 45, and which may be given as $[\alpha]^{20}_{D} = 22.10$. 20 grams of Rochelle salt with 5, 10, 15, or 20 grams of different alkali salts were dissolved to make 100 cc. of solution and the variations, Δ, from the value 22.10 were determined. These were found to be partly positive and partly negative, and increased with increased amounts of the alkali salts. In the following table the results are given which were found with 5 and 20 grams of the salts (or with other amounts designated in parentheses) :

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[1] Hammerschmidt : *Loc cit.*, p. 22.

[2] Long: Am. J. Sci. Arts, [3], 36, 351 (1888)

Increase in 22.10 by Δ			Decrease in 22 10 by Δ.		
Given by	Amount of salt		Given by	Amount of salt	
	5 grams	20 grams		5 grams.	20 grams.
	Δ	Δ		Δ	Δ
KCl	0.62	1.33	$NaCl$	0.30	2.35
KBr	0.62	1.01	$NaBr$	0 21	1 00
KI	0.19	0.85	$NaNO_3$	0.38	1.03
KNO_3	0.36	1.37	Na_2SO_4	0 43	1.60
K_2SO_4	0.50	0.63 (10)	$Na_2HPO_4 + 12 aq$	0.19	0.52
$KSCN$	0.38	0.73	$NaH_2PO_2 + aq$	0.20	1.78
$KC_2H_3O_2$	0.42	1 02	$Na_2S_2O_3 + 5 aq$	0 24	1.19
$K_2C_2O_4 + aq$	0 47	..	$NaC_2H_3O_2 + 3 aq$	0.15	0 98
			$Na_2B_4O_7 + 10 aq$	..	0.28 (10)
NH_4Cl	0 48	1.00	Na_2WO_4	.	1 41 (10)
HH_4Br	0 37	0.63 (15)			
NH_4SCN	..	0.49 (10)	$LiCl$	1.67 (6.75)	..
$(NH_4)_2C_2O_4 + aq$	0 41	..	Tl_2SO_4	3.43	..

The specific rotation of potassium sodium tartrate is accordingly increased, in the concentrations employed, by addition of potassium or ammonium salts, while, on the other hand, sodium salts, lithium chloride, and thallium sulphate cause a decrease. The reason for these opposite actions is not clear, and no investigations have been made to show whether or not they hold good in dilute solutions The strongest effect is found with thallium sulphate.

Neutral potassium tartrate also, as shown by Schütt,[1] exhibits a slight increase in specific rotation by addition of potassium chloride, and a decrease with sodium chloride. The following mixtures were made and the polarization, *p*, found in a 2-dm. tube with a half-shadow instrument having the Ventzke sugar scale. From these values the specific rotations $[\alpha]_D$ were calculated:[2]

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[1] Schütt Ber d chem Ges., 21, 2586.

[2] On the assumption that 1° Ventzke (ray *j*) = 0 346 angular degree (ray *D*).

In 100 cc solution.	P	Diff	$[\alpha]_D$.	Diff.
40 gm. tartrate + 8 gm. KCl...	66.8	1.0	28.89	0.43
40 " "	65.8	3.0	28.46	1.30
40 " " + 8 gm. NaCl...	62.8		27.16	
30 gm. tartrate + 14 gm KCl..	49.9	1.2	28.78	0.70
30 " "	48.7	4.0	28.08	2.30
30 " " + 14 gm. NaCl..	44.7		25.78	
20 gm. tartrate + 22 gm KCl..	33.3	1.5	28.80	1.29
20 " "	31.8	4.3	27.51	3.72
20 " " + 22 gm NaCl..	27.5		23.79	
10 gm. tartrate + 25 gm KCl..	16.7	1.1	28.89	1.90
10 " "	15.6	2.4	26.99	4.15
10 " " + 25 gm. NaCl .	13.2		22.84	

The effect varies with the proportions in which the substances are mixed. On this difference in behavior of potassium chloride and sodium chloride Schutt has based a method for the quantitative analysis of a mixture of the two salts. See Part V.

A slight decrease in the rotation of sodium tartrate by addition of sodium nitrate was observed by Th Thomsen.[1]

The specific rotation of tartar emetic ($K.SbO.C_4H_4O_6\frac{1}{2}H_2O$) for $c = 5$, $[\alpha]^{20} = + 141.27$, was found by Long[2] to be diminished by addition of potassium, sodium and ammonium salts, and in greater degree, the more of the salts are present. The decrease by KCl, KBr, KNO_3, $NaCl$, $NaNO_3$, NH_4Cl, and NH_4NO_3 is slight, while for sodium acetate, sodium phosphate, and sodium carbonate it is considerable, when these salts are added in amount insufficient to produce a precipitate. Thus, 10 grams of sodium acetate reduce the specific rotation given above to 123.59, and small amounts of sodium carbonate to 55.8 even. According to Long, the action of these salts depends on this, that the antimonyl-potassium tartrate is partly decomposed into alkali tartrates and compounds containing SbO and K with acetic, phosphoric, and carbonic acids.

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[1] Thomsen: J. prakt. Chem, [2], 34, 83.

[2] Long: Am. J. Sci. Arts, [3], 38, 264; 40, 275.

b Influence of Boric Acid on the Rotation of Tartaric Acid.—The marked increase in activity which is found here was observed first by Biot[1] in 1837 and later made the subject of lengthy investigations.[2] In order to follow the changes which occur where water and boric acid are both added, he showed first that the rotation of the tartaric acid is increased by each one of these bodies taken alone; that is, first, by melting the tartaric acid with increasing amounts of boric acid to form glass-like masses, and secondly, by dissolving the acid in increasing quantities of water. If now an aqueous solution of tartaric acid be treated with boric acid, the observed specific rotation depends on these two conditions:

1 On the relation of the tartaric acid to the boric acid. The latter increases the rotation, as borotartaric acid is formed, and this has a greater rotating power.[3] If the relation of tartaric acid to water is maintained constant, the increase which the specific rotation of tartaric acid experiences by addition of varying amounts of boric acid, β, may be expressed by the formula

$$[\alpha] = A + \frac{B\beta}{C + \beta},$$

in which the constants, A, B, C, are to be found by a series of observations

2. On the amount of water On the one hand, this acts to increase the rotation of the tartaric acid, but on the other, it causes hydrolytic decomposition of the borotartaric acid, and in consequence, a decrease in the rotating power. Experiments showed that as long as the mixture contained for 1 part of tartaric acid less than 0.088 part of boric acid, the rotation is increased by gradual increase in the amount of water. If the relation between tartaric acid and boric acid is exactly 1 : 0.088, the specific rotation remains the same for all dilutions, because then, through the increasing hydrolysis of the borotartaric acid, the activity is decreased in the same degree in which it would be increased by the influence of the

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[1] Biot · Mem de l'Acad, **16**, 229

[2] Biot: Ann chim phys, [3], **11**, 82 (1844), **29**, 341, 430 (1850), **59**, 229 (1860).

[3] Mono- or diboryltartaric acid Not stable in solid condition. (Duve Jahresbericht, 1869, p 540) Dubrunfaut, Compt rend, **42**, 112, assumes the formation of the compound, $H_3BO_3 + 2C_4H_6O_6$

dded water on the tartaric acid. Finally, if the mixture contains, for 1 part of tartaric acid, more than 0.088 part of boric acid, then the first action is the stronger and the rotation alls by increasing addition of water. In general, in these cases, the changes may be expressed by the formula $[\alpha] = A + Bq$, in which q represents the amount of water n 100 parts by weight of the mixture If all three components are varied, a maximum rotation is found for definite weight relations. The papers of Biot contain a large amount of numerical data, which are based on red light with a wave-ength of about 635 $\mu\mu$.

With reference to the D ray, for which but few investigations have been made, the extent of the influence of boric acid on the specific rotation of tartaric acid may be seen from he following numbers (Koch):[1]

In 100 cc of solution		Mol relation.		$[\alpha]_D$ of the tartaric acid	
Tartaric acid Grams	Boric acid Grams	Tartaric acid	Boric acid	With boric acid	Without boric acid
32 13	3 32	4	1	+ 29 80°	+ 10.86°
29 11	4 01	3	1	34.09	11 25
24 51	5 06	2	1	39.58	11 85
16 63	6 87	1	1	43 44	12 88

By determining the electrical conductivity of a large number of different mixtures of tartaric acid, boric acid, and water, Magnanini[2] also was able to prove the existence of a boroartaric acid compound, which conducts well, and the electroytic dissociation of the same by increasing addition of water

On the rotation of the alkali boryl tartrates see § 61.

Magnanini found that other oxy-acids also experience an increase in conductivity by addition of boric acid; thus, lactic acid, glyceric acid, oxybutyric acid, and malic acid[3] An increase in optical activity might be expected therefore with these, which, with reference to malic acid, was already pointed out by Pasteur.[4]

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[1] P. Koch· "Einwirkung weinsaurer Verbindungen auf polarisirtes Licht" Inaug.-Diss., Tübingen 1869.

[2] Magnanini: Zeit. phys. Chem, **6**, 67; Gazz chim ital, **20**, 453; **21**, II, 134

[3] Magnanini: Gazz. chim. ital., **21**, II, 215. Ber. d. chem. Ges., **24**, III, 894

[4] Pasteur: Ann. chim. phys., [3], **59**, 243

c. Action of Molybdates and Tungstates on Tartaric Acid.— On this question extended investigations have been carried out by Gernez which cover the following salts:

Sodium molybdate……	$Na_2MoO_4 + 2$ Aq, Compt. rend., 104, 783.
Lithium molybdate…..	Li_2MoO_4, Compt. rend., 108, 942.
Magnesium molybdate..	$MgMoO_4$, Compt. rend., 108, 942.
Ammonium molybdate..	$(NH_4)_6Mo_7O_{24} + 4$ Aq, Compt. rend., 105, 803.
Potassium tungstate….	K_2WO_4, Compt. rend., 106, 1529.
Sodium tungstate…….	$Na_2WO_4 + 2$ Aq, Compt. rend., 106, 1527.

In these investigations, solutions were employed which contained always in 100 cc., 2.5 grams of tartaric acid and increasing amounts of the salts, added in molecular proportions to the tartaric acid. Gernez reports only the angles of rotation found in a tube 1.057 dm. in length. The following table contains the complete numerical data for ammonium molybdate, and in the last column, the specific rotations (calculated by Dr. Berndt), which correspond to the tartaric acid in the different solutions.

AMMONIUM MOLYBDATE.

Mol of salt to 1 mol of tartaric acid in $^1/_{128}$ mol	Grams of salt to 2.5 grams of tartaric acid	α_D^{17} for $l = 1.057$ dm	$[\alpha]_D^{17}$
0	0.000	0° 21′	+ 13.2°
1	0.161	1 2	39.0
2	0.322	1 41	63.6
3	0.482	2 21	88.9
4	0.644	2 57	112
6	0.965	4 5	154
8	1.288	5 3	191
12	1.931	6 52	260
16	2.575	8 49	334
24	3.863	13 22	506
32 = $^1/_4$	5.150	17 38	667
40	6.438	19 50	750
42.66 = $^1/_3$	6.866	20 39*	781*
48	7.725	20 36	780
56	9.013	20 35	779
64 = $^1/_2$	10.300	19 47	749
96	15.450	17 28	661
128 = 1	20.600	16 44	633
192 = $1^1/_2$	30.900	16 33	626

For the other salts Dr. Berndt has calculated the following specific rotations of tartaric acid from the data of Gernez:

Added salt in $^1/_{12}$ mol for each mol of tartaric acid.	Tungstate of		Molybdate of		
	Potassium $[\alpha]_D^{16}$	Sodium. $[\alpha]_D^{16}$	Sodium. $[\alpha]_D^{17}$	Lithium. $[\alpha]_D^{16}$	Magnesium. $[\alpha]_D^{16}$
0	14.0°	14.0°	13.2°	14.0°	14.0°
$^1/_2 = {}^1/_{24}$ mol	28.4	27.6	31.4	25.3	23 4
$1 = {}^1/_{12}$ "	41 6	40.5	51.1	38.6	33.3
$2 = {}^1/_6$ "	69 3	65 6	89 7	62.4	53 3
$3 = {}^1/_4$ "	95.4	91.6	128	87 7	72.2
$4 = {}^1/_3$ "	119	117	167	112	91 5
5	143	141	206	137	110
$6 = {}^1/_2$ "	169	164	243	162	129
7	196	185	288	186	149
8	223	207	334	209	169
9	252	228	383	235	189
10	281	247	435	255	209
11	308	264	479	277	229
12 = 1 "	327*	277*	517*	299	248
13	318	271		330	272
14		.	513	358	294
15	270	241	512	383	318
16	..			413	343
17	.			438	368
18	241	222	505	462	394
21	..	210		483	463
24 = 2 "	211	199	498	484*	523*
36 = 3 "		170	482	468	509
48 = 4 "	.	154	473	457	495
60 = 5 "	.	140	455	450	478

It is seen, therefore, that the specific rotation of tartaric acid increases on addition of increasing amounts of the salts to a maximum, after which a decrease follows which is marked with the tungstates, but slight with the molybdates. These maximum points correspond to definite molecular proportions between the tartaric acid and the salts, and in fact to

3 $C_4H_6O_6$: 1 $(NH_4)_6Mo_7O_{24}$ + 4 aq
1 " · 1 K_2WO_4
1 " · 1 Na_2WO_4 + 2 aq
1 " : 1 Na_2MoO_4 + 2 aq
1 " : 2 Li_2MoO_4
1 " : 2 $MgMoO_4$

The remarkably great increase in the specific rotation of tartaric acid, which, for example, with ammonium molybdate reaches a value sixty times the original, may be, without doubt, ascribed to the formation of complex acids. Rosenheim[1] has already shown that tungstic, molybdic, and vanadic acids form such compounds with oxalic acid.

d. Action of Molybdates and Tungstates on Ordinary Malic Acid—Investigations on this point are also due to Gernez. They deal first with the behavior of

Ammonium molybdate···	$(NH_4)_6Mo_7O_{24}$ + 4 Aq,	Compt. rend., 109, 151.
Sodium molybdate······	Na_2MoO_4 + 2 Aq,	Compt rend., 109, 769.

In each case 1 1166 grams of malic acid were dissolved with increasing amounts of the salts, *P*, to make 12 cc., and the angle of rotation, α_D, was found in a tube 1.057 dm long at a temperature of 17°. The following table does not give all the solutions tested by Gernez, but only those with the numbers added; in the fourth column the specific rotations of the malic acid, calculated by Dr Berndt, are given

Ammonium molybdate					Sodium molybdate				
No of solution	Grams salt *P*	α^{17}_{D}.	$[\alpha]^{17}_{D}$.	*Z*	No of solution	Grams salt *P*	α^{17}_{D}.	$[\alpha]^{17}_{D}$	*Z*
1	0 000	— 0 20°	— 2.0°		1	0 000	— 0 20°	— 2 0°	
2	0 013	— 0.40	— 4.1		3	0.084	— 1.12	— 11.4	
4	0.054	— 0 97	— 9.9		5	0.336	— 3 72	— 37 8	
5	0 107	— 1.70	— 17.3		6	0.504	— 5 48	— 55.7	
6	0 191	— 2 75	— 28 0		7	0.672	— 7 25	— 73.7	
8	0 282	— 3 82	— 38.8		9	1.008[6]	— 9 07	— 92.1	M_1
10	0 429	— 4.95	— 50 3		10	1.176	— 5.20	— 52.9	
14	0 572[2]	— 5 32	— 54 1	M_1	11	1 344	— 1 52	— 15 5	
16	0.644	— 4.93	— 50 1		12	1.513	+ 3 02	+ 30.7	R_1
18	0.736	— 4 17	— 42 4		14	1.848	+ 11 03	+ 112 2	
20	0.792	— 3 40	— 34.6		15	2.017[7]	+ 14 02	+ 142 5	M_2
22	0 936	— 1.00	— 10.2		17	2.353	+ 8 68	+ 88.2	
23	0 966	— 0.42	— 4.3	*R*	19	2.689	+ 2.62	+ 26.6	
24	1.030[3]	+ 0.83	+ 8.4		20	2 857	+ 0.32	+ 3.3	
26	1.144	+ 3.23	+ 32.8		21	3.025[8]	— 0.83	— 8.4	R_2
28	1.288	+ 7.20	+ 73.2		24	3.529[9]	— 1.55	— 15.8	M_3
29	1 395	+ 10 35	+ 105.3		26	3.865	— 1.00	— 10.2	
32	1.717[4]	+ 20 92	+ 212 7		27	4.033[10]	— 0.50	— 5.1	
36	2.146	+ 36 22	+ 368 2		28	4.201	0.00	0.0	R_3
40	2.575[5]	+ 52.47	+ 533 5		30	4.538	+ 0.87	+ 8.8	
43	3 863	+ 72.00	+ 731 9		32	5.042	+ 2.27	+ 19.3	
46	5.150[6]	+ 72.80	+ 740 1	M_2	36	5.546	+ 3.95	+ 40 2	
48	6.008	+ 72.33	+ 735 3		39	7.058	+ 7.17	+ 72.9	
49	6 438	+ 72 00	+ 731.9		41	8 067[11]	+ 10.25	+ 104.2	

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[1] Rosenheim Ztschr anorg Chem, 4, 352, Ber d chem. Ges, 26, II, 1191.

[2] Equals 1/18 mol

[3] Equals 1/10 mol.

[4] Equals 1/6 mol

[5] Equals 1/4 mol

[6] Equals 1/2 mol

[7] Equals 1 mol

[8] Equals 1 5 mols.

[9] Equals 1 75 mols.

[10] Equals 2 mols.

[11] Equals 4 mols.

From the above, it is evident that the relations are much more complicated than with tartaric acid, inasmuch as shown by the letters under *Z*, not only are there points of maximum rotation (*M*) but points of change in the direction of rotation or reversal *R*; increasing amounts of *ammonium molybdate* cause at first an increase in the original levorotation which grows to a maximum, then decreases, and finally changes to dextrorotation which increases very rapidly, but at last falls a little. With *sodium molybdate* there are found three inactive concentrations and three points of maximum rotation of which two are on the side of levorotation, and one on that of dextrorotation. The curve expressing these changes would have a zigzag form. Finally, it may be remarked that the characteristic points, *M* and *R*, frequently correspond to concentrations at which there is a definite molecular relation between the malic acid and added salts.

Further investigations of Gernez are concerned with the action of the following salts on the rotation of malic acid

Potassium tungstate	K_2WO_4	Compt rend, 110, 1365.
Sodium tungstate	Na_2WO_4	
Lithium molybdate	Li_2MoO_4	Compt. rend, 110, 529
Magnesium molybdate	$MgMoO_4$	
Sodium potassium molybdate	$K_2Na_4Mo_8O_{12} + 14\ Aq$	Compt rend, 111, 792
Acid sodium molybdate	$Na_6Mo_7O_{24} + 22\ Aq$	
Potassium phosphomolybdate	$K_8P_2Mo_5O_{24}$	Compt rend, 112, 226
Sodium phosphomolybdate	$Na_6P_2Mo_5O_{23} + 14\ Aq$	
Ammonium phosphomolybdate	$(NH_4)_6P_2Mo_5O_{23}$	

The relations appearing here, are, in general, similar to those found with sodium and ammonium molybdates.

B Sugars.

a. Changes in the Rotation of Cane-Sugar by Alkalies and Salts.—As a great many investigations, carried out largely with reference to saccharimetry have shown, the following bodies all cause a decrease in the rotation:

Hydroxides of the alkali and alkali-earth metals.

Chlorides, nitrates, sulphates, carbonates, phosphates, acetates and citrates of the alkali metals.

Borax,

Magnesium sulphate,

Chlorides of the alkali-earth metals.

The action of these substances increases with increased addition of the same, and so as to reduce the specific rotation of cane-sugar from + 66.7° to about 60°.[1]

On the behavior of the chlorides of the alkali and alkali-earth metals, the extended experiments of Farnsteiner[2] have given the following specific rotations $[\alpha]_D$:

	1 Part of cane-sugar and			
	Parts of salt.	Parts of water.		
		3	5	10
Without salt		66.60°	66.67°	66.75°
KCl	1.083	63.55	64.55	..
NaCl	1.004	62.47	63.80	..
LiCl	1.008	61.57	63.18	..
$BaCl_2$	1.030	65.95	66.10	66.35
$SrCl_2$	1.096	64.12	65.00	65.85
$CaCl_2$	0.996	63.52	64.42	..
$MgCl_2$	1.230	62.17	63.70	65.30

The effect of the salts becomes weaker with increased dilution. It is further evident that the decrease in rotation brought about by nearly equal weights of salts is greater, the lower the molecular weight of the chloride.

Borax, like the other alkali salts, causes a decrease in the specific rotation of cane-sugar. Müntz[3] found the following values when he examined solutions obtained by mixing 10 grams of cane-sugar in 100 cc. with increasing weights of borax:

Borax =	0	0.5	1	2	3	4	5	7.5 grams
$[\alpha]_D$ =	66.7	65.9	65.0	63.5	62.5	61.6	61.1	60.5°

The effect of increased addition of salts has been followed in most cases only to a low limit. More extended investigations have been carried out by Farnsteiner[4] with reference to calcium chloride, and these have shown that following the first observed decrease in the rotation, an increase later appears, when the salt addition passes a certain limit. To a solution of 1 part of sugar in 8.643 parts of water, the following amounts of calcium chloride were added:

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[1] A complete compilation of observations is found in Lippmann's "Chemie der Zuckerarten."

[2] Farnsteiner. Ber d chem. Ges, 23, II, 3570.

[3] Muntz: Ztschr. Rübenzuker-Ind., 26, 735.

[4] Farnsteiner Ber. d. chem. Ges., 23, 3572.

No. of the sol.	1	2	3	4	5
$CaCl_2$	0	0.955	1.719	2.753	2.998 parts
$[\alpha]_D^{17.5}$	66.74	65.41	64.50	63.50	63.41
No of the sol	6	7	8	9	10
$CaCl_2$	3.646	4.195	5.356	5.676	5.987 parts
$[\alpha]_D^{17.5}$	63.23*	63.45	65.66	66.35	67.88

The minimum (*) of rotation is found with solution No. 6. In solution No. 10 the sugar shows a stronger specific rotation than it does without addition of salt.

It has been observed with ammonia also that in its concentrated solutions (16 to 24 per cent. NH_3) it occasions an increase in the rotation of sugar, while in dilute solution it produces a very small, or possibly even no, decrease (Ost)[1]

b Dextrose and Calcium Chloride.—It has been observed here that the rotation is increased by addition of the salt Rimbach[2] found the following values for $[\alpha]_D$:

Strength of the $CaCl_2$ solution used Per cent.	Dextrose in 100 parts by weight of the whole solution			
	30	20	10	5
0.00	55.0°	55.4°	55.8°	56.1°
10.02	55.6	55.5	54.8	54.9
19.94	60.7	60.5	60.1	60.4

With the 5 and 10 per cent. dextrose solutions a slight decrease in the rotations is at first observed.

c. Action of Borax on Bodies of the Mannitol Group.—While, as remarked above, the effect of borax is to decrease the rotation of cane-sugar, it produces an increase of rotation in the alcohols of the glucose group. The phenomenon was first observed by Vignon with mannitol, and later E. Fischer found the same behavior in the pentitols, hexitols, etc., discovered by him. Many of these bodies, which from their constitution should be active and which are not racemes, show in pure aqueous solution either no rotation or a very small one, but this may be developed by addition of borax to the solution. The extent of the rotation caused in this way may be seen from the table below, the specific rotations being calculated in most cases from the data in the original papers:

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[1] Ost: Neue Ztschr. für Rübenzucker-Ind., 9, 41.

[2] Rimbach: Ztschr. phys. Chem., 9, 707.

	Without borax. $[\alpha]_D$	With borax In 100 cc solution			Observer
		Sugar.	Borax.	$[\alpha]_D$	
l-Arabitol	0	10.38	7.3[4]	4.8	Fischer[5]
d-Mannitol	0 [−0.25][1]	10	12.8	+22.5	Vignon[6]
d- "	"	3	7.4	+28.3	Fischer[7]
l- "	"	3	7.4	28.3	"
d-Sorbitol	0 [−2.04][2]	9.06	7.3	+1.5	v. Lippmann[8]
d- "	"	9.06	7.3	+1.4	Fischer and Stahel[9]
l- "	"	9.06	7.3	1.4	" "
d-Talitol...........	+2.3	10	7.3	5.5	Fischer[10]
α-Mannoheptitol (Perseït) ..	−1.22[3]	8	7.3	+4.8	Fischer and Passmore[11]
α-Glucooctitol......	+2.0	10.53	10	+6.0	Fischer[12]
β-Methylgalactoside	0	10	10	+2.6	" [13]

In ordinary *d*-mannitol dissolved in water Vignon,[14] Muntz and Aubin,[15] and others could find no activity, but Bouchardat,[16] the other hand, with a tube three meters in length filled th a solution of $c = 15$, found by aid of a half-shadow paratus and sodium light a rotation $\alpha_D = -1° 8'$, from ich $[\alpha]_D = -0.25°$. Under similar conditions it is likely at rotating power would be found in solutions of other bodies the mannitol group.

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[1] Bouchardat: Compt. rend., 80, 120: Jahresbericht, (1875), p 148

[2] Gernez. Compt rend., 113, 1031.

[3] Gernez *Ibid.*, 114, 480.

[4] Amount in a borax solution saturated at the ordinary temperature

[5] Fischer: Ber. d. chem Ges., 24, 538.

[6] Vignon · Compt. rend., 77, 1191 (1873); Ann. chim. phys., [5], 2, 440 (1874)

[7] Fischer Ber. d chem. Ges, 23, 385.

[8] v. Lippmann: *Ibid.*, 25, 3220.

[9] Fischer and Stahel. *Ibid.*, 24, 2144.

[10] Fischer *Ibid.*, 27, 1528.

[11] Fischer and Passmore · *Ibid.*, 23, 2232.

[12] Fischer: Ann. Chem. (Liebig), 270, 99.

[13] Fischer · Ber. d. chem Ges., 28, 1155.

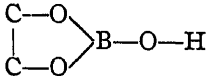
[14] Vignon. *Loc. cit.*

[15] Müntz and Aubin: Ann. chim. phys., [5], 10, 533.

[16] Bouchardat: Compt. rend., 80, 120.

The chemical action of borax on the compounds of the nnitol group does not consist in the formation of simple dition products. It is known that not only these varieties sugars but also the glucoses, as grape-sugar, galactose, ctose, and even glycol and glycerol on addition of borax, ich in itself has an alkaline reaction, yield strongly acid utions and this is also the case when sodium bicarbonate ut not the mono-carbonate) is likewise present (Dunstan,[1] ein,[2] Lambert,[3] Donath,[4] Jehn)[5]

It appears that, as with the oxyacids (tartaric acid), bodies acid character containing boron are formed, which, in conquence of the reaction of two hydroxyl groups on one molele of boric acid, contain the cyclic complex



(van't Hoff)[6]

If free boric acid is added to mannitol the two unite in the oportion of 3 molecules of acid to 1 of mannitol, as Magnini[7] found by observations on the electric conductivity of eir solutions

The sugars, which from their constitution should be inactive, not become active by addition of borax, which has been own for dulcitol (Crossley),[8] xylitol (Fischer),[9] adonitol ischer),[10] and α-glucoheptitol (Fischer)[11]

Other bodies also besides borax have the power to call out e activity of mannitol. Thus, right rotation is produced by arsenic acid, neutral sodium arsenate (Vignon),[1] tungstates (Klein).[2] Left rotation is produced by alkalies, alkali carbonates, acid sodium arsenate and alkali-earths (Vignon).

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[1] Dunstan Ber. d. chem Ges, 16, 2504 Ref

[2] Klein· Compt. rend, 99, 144; Bull Soc Chim [2], 29, 198, 357. It is said that the ium salt, $(C_6H_{12}O_6)_2BaO\ 2B_2O_3$, can be made

[3] Lambert Compt rend., 108, 1016

[4] Donath· Chem. Ztg., 17, 1826.

[5] Jehn: Arch. Pharm, 25, 250, 26, 495

[6] van't Hoff: Lagerung der Atome in Raume, 2nd ed., p. 113

[7] Magnanini Ztschr. phys Chem, 6, 66.

[8] Crossley: Ber. d. chem. Ges., 25, 2564.

[9] Fischer: *Ibid.*, 24, 528.

[10] Fischer: *Ibid.*, 26, 634.

[11] Fischer: Ann. Chem. (Liebig), 270, 81.

d. Action of Acid Sodium and Ammonium Molybdate on Mannitol, Sorbitol, α-Mannoheptitol (Perseït) and Rhamnose (Isodulcitol).– The three sugars named first, which in pure aqueous solution possess a slight rotation to the left, are not influenced by neutral molybdates; on the other hand free molybdic acid and its acid salts produce in these solutions strong dextrorotation. Gernez added the molybdates,

$$Na_6Mo_7O_{24} + 22H_2O \text{ and } (NH_4)_6Mo_7O_{24} + 4H_2O,$$

in increasing amounts ($\frac{1}{24}$ to above $\frac{12}{24}$ of the molecular weight to 1 mol. of sugar) and found that the right rotation increases to a maximum and then decreases. The largest values for mannitol sorbitol and mannoheptitol, were found when the solutions contained for one molecule of these bodies $\frac{6.75}{24} = 0.28$ molecule of the sodium or ammonium molybdate. The following specific rotations are calculated from the data of Gernez.[3]

	Sugar in 100 cc. solution.	Temp.	Rotation of the pure aqueous solution. $[\alpha]_D$	Maximum rotation With $\frac{6.75}{24}$ mol salt added Na salt $[\alpha]_D$	NH₄ salt $[\alpha]$
d-Mannitol	3.160	17°	0.26°	+ 43.19	+ 43.14
d-Sorbitol ..	6.548	17	2.04	+ 41.87	+ 41.48
d-Perseït ...	7.361[4]	15	1.22	+ 48.77	+ 48.[illegible]

The behavior of rhamnose is somewhat different.[5] This body shows immediately after solution in water a rotation to the left, then after some hours a constant right rotation which has, for $c = 6.319$, the value $[\alpha]_D^{18} = +9.75°$. This last is increased by addition of sodium or ammonium molybdate until the salt added amounts to $\frac{6.75}{24}$ molecule for each molecule of rhamnose, and then remains unchanged with further addition of the salts. The observed constant maximum rotation amounts to

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[1] Vignon: Ann. chim. phys., [5], 2, 433.

[2] Klein: Compt. rend., 89, 484.

[3] Gernez. Mannitol, Compt. rend., 112, 1360. In this paper the maximum of rotation is given for $\frac{6.75}{24}$ molecule of the salt, although the half weight of the above formula appears to have been taken. Sorbitol, Compt. rend., 113, 1031; Perseït, *Ibid.*, 114, [illegible]

[4] Superaturated.

[5] Gernez: Rhamnose, Compt. rend., 119, 63.

$$[\alpha]_D^{18} = +22.95°, \text{ for the sodium salt,}$$
$$[\alpha]_D^{18} = +19.91°, \text{ for the ammonium salt}$$

A satisfactory explanation for the occurrence of the number $\frac{17.5}{24}$ is wanting. Possibly, as with borax, the molybdenum enters the sugar molecule.

F. Multirotation.

With a number of active substances the phenomenon is observed that the rotating power of a freshly prepared solution changes on standing, undergoing either an increase or decrease until finally a constant value is reached This behavior is shown by

1. A number of the sugars.
2. Certain oxy-salts and their lactones.
3. A few other substances

I Multirotation of the Sugars

71. **Preliminary Remarks.**—In 1846 Dubrunfaut[1] made the observation that the rotation of an aqueous grape sugar solu- ion, prepared at the ordinary temperature, decreased to a cer- ain limit on standing The same behavior was noted in 1850 y Pasteur[2] in a grape-sugar-sodium chloride solution, and this hemist established the fact that the beginning rotation is bout twice as great as the final constant rotation, a condition which E. O Erdmann[3] in 1855 and Dubrunfaut[4] in 1856 veri- ied with grape-sugar. The high beginning rotation was, there- ore, designated as *birotation*

The phenomenon of decrease in rotation was noted by Erdmann in ordinary milk-sugar, and later the same behavior as been observed by Tollens and E. Fischer in many other arieties of sugars It has been recognized, however, that the elation of the beginning to the final rotation is not always 2 : 1, s with dextrose, but may be 1.6 : 1 as in the case of milk- ugar, or 1.46 : 1 as with galactose or 4.67 : 1 as observed with xylose. Because of this it was suggested by Wheeler and Tollens[1] in 1889 to change the first designation, *birotation*, into *multirotation*.

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[1] Dubrunfaut: Compt rend , **23**, 42

[2] Pasteur: Ann. chim. phys., [3], **31**, 95

[3] Erdmann. Jahresbericht, (1855), p 671.

[4] Dubrunfaut: Compt rend., **42**, 228.

It was further observed by Schmöger[2] in 1880 and also by E. O. Erdmann[3] that milk-sugar on dehydration changes into a modification which on re-solution shows a gradual increase in rotation and the same behavior was found with maltose by Meissl[4] in 1882. Schmöger describes this low rotation as *half rotation*. The terms *greater rotation* (Mehrdrehung) and *less rotation* (Wenigerdrehung) were later introduced by Parcus and Tollens[5] to describe the two kinds of rotation.

A further advance was made in 1895 by Tanret who found that in certain sugars, besides the known modifications, α and β, of which the higher rotating, α, is transformed after solution into β, a third modification, γ, may be obtained which in solution is likewise transformed into β This is the case in the following bodies, the three forms of which with respect to their specific rotations, $[\alpha]_D$, stand in the following order, $\alpha > \beta > \gamma$.

Modification	α (labile)	β (stable)	γ (labile)
d-Glucose	$> + 105^\circ$	$+ 52.5^\circ$	$< + 22.5^\circ$
d-Galactose...	$> + 135$	$+ 81$	$< + 52$
Milk-sugar	$> + 88$	$+ 55$	$< + 36$

The form α shows greater rotation and γ less rotation; there is then by the change of α into β a decrease and, on the other hand, by the change of γ into β an increase in the rotation

The conditions with rhamnose are different.

Modification	α	β	γ
Rhamnose	$< - 6^\circ$	$+ 9^\circ$	$> + 23^\circ$

Here we find by the conversion of α into β, first a decrease in the negative rotation, and then after passing a certain point of inactivity, an increase in the right-hand rotation, while the change of γ into β is accompanied by a decrease in rotation. The preparation of the three modifications of the above sugars is given in § 72.

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[1] Wheeler and Tollens Ann Chem (Liebig), **254**, 312
[2] Schmöger· Ber. d chem Ges, **13**, 1915
[3] Erdmann· Ber. d chem. Ges, **13**, 2180
[4] Meissl J prakt Chem., [2], **25**, 122
[5] Parcus and Tollens Ann Chem (Liebig), **257**, 161

The rapidity with which a labile modification of a sugar changes into the stable form, increases in marked degree with rise in temperature. At the ordinary temperature a period of from six to twenty-four hours is usually required, but by boiling, the transformation is completed in a few minutes. This behavior was observed by Dubrunfaut with grape-sugar and with milk-sugar.

After solution of a labile sugar form in water the change begins immediately and it is not, therefore, possible to establish the beginning rotation with accuracy. Several minutes must elapse before the observation of the liquid in the polariscope can commence, and with the *greater rotating* α-forms a value somewhat too low and with the *lower rotating* γ-forms a value somewhat too high is always found. An accurate result is obtained only for the end product of the transformation, the stable β modification

72. Resume of the Sugars Showing Multirotation.—The following observations were all carried out by allowing the transformation to proceed at the ordinary temperature (usually 20°) First in the shortest possible time after preparation of the solutions, the beginning rotation was determined and later the constant end rotation, the time required to complete the change being noted The specific rotations given correspond to $[\alpha]_D$, and the concentration, *c*, expresses the number of grams of sugar in 100 cc. of solution.[1]

I *l-Arabinose*, $C_5H_{10}O_5$ (two modifications)

α-Modification. Ordinary crystallized arabinose.

β-Modification.—This is obtained by precipitating a hot solution of the α-form in an equal weight of water, by addition of 20 parts of absolute alcohol. In the crystallized condition it is not stable and reverts gradually to the α-form.[2]

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[1] Many of the data based on density and percentage composition have been reduced to this form to correspond.

[2] Tanret Bull. Soc. Chim., [3], 15, 201.

Observed for $c = 9.73$, $l = 20$

α. First rotation after 6.5 minutes	+156.7°	} Decrease
β. Final rotation after 1.5 hours	+104.6°	} 52.1°

β. ($c = 13.8$) +105°. ($c = 2.5$) = +104° (Tanret)

2. *l-Xylose*, $C_5H_{10}O_5$ (two modifications)

α-Modification, ordinary xylose.

β-Modification, not yet obtained pure, but mixed with α, reverts to α in solid condition.

Observation 1. $c = 10.235$, $l = 20$

α. First rotation after 5 minutes................	85.9°	} Decrease
β. Final rotation after 5 hours	18.6°	} 67.3

Observation 2. $c = 11.07$, $l = 20$

α First rotation after 4.5 minutes	78.6°	} Decrease
β. Final rotation after 2.5 hours	19.2°	} 59.4

✓ 3. *d-Glucose*, $C_6H_{12}O_6$ (three modifications)

α-Modification.—Ordinary form crystallized from water at mean room temperature as hydrate, $C_6H_{12}O_6 + H_2O$, or as anhydrous crystallized grape sugar from alcohol or from water at 30° to 35°. Immediately after solution, and referred to the anhydride, $[\alpha]_D = +105°$, then by change into β, decreases to 52.5.

β-Modification. This remains usually as an amorphous hygroscopic mass by evaporation of dissolved α-glucose. It may be obtained in crystalline condition by evaporating on the water-bath, and stirring constantly, dissolving the residue dried at 98° in half its weight of cold water and adding a large amount of alcohol cooled to 0°; or it may be made by melting α-glucose, cooling to 100° and adding some crystals of β-glucose. It dissolves at 19° in half its weight of water and shows the constant rotation of +52.5° (referred to $C_6H_{12}O_6$). On evaporation of its aqueous solution it yields α-glucose, which, however, is only formed after crystallization, as the mother-liquor shows always the rotation of β.[4]

The *γ-Modification* is formed when a concentrated solution

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[1] Parcus and Tollens: Ann. Chem. (Liebig), 257, 174.

[2] Wheeler and Tollens: Ann. Chem. (Liebig), 254, 311.

[3] Parcus and Tollens: Ann. Chem. (Liebig), 257, 175.

[4] According to Lobry de Bruyn and Alberda van Ekenstein: Ber. d. chem. Ges., 28, 3082.

of α-glucose is evaporated and the residue heated for several hours to 110°. The mass, which consists of β and γ, is dissolved in an equal weight of water and treated with a large volume of alcohol which precipitates the γ-form first. This form separates first also by recrystallizing from alcohol. It requires for solution at 19°, three-fourths of its weight of water and shows a beginning rotation of + 22.5° (for $C_6H_{12}O_6$) which, in consequence of change to the β-modification increases gradually to 52.5°.[1]

The three forms exhibit the same depression of the freezing-point.

Change of α into β.

1. $c = 9.097$, $t = 20°$

α	First rotation after 5.5 minutes	+ 105.2°	Decrease 52.7°
β	Final rotation after 6 hours	+ 52.5°	

2. $c = 5.526$, $t = 20°$.

α	First rotation after 7 minutes	+ 104.3°	Decrease 51.7°
β	Final rotation after 7 hours	+ 52.6°[2]	

Change of γ into β

γ	First rotation (Tanret)	+ 22.5°	Increase 30.0°
β	Final rotation	+ 52.5°	

4. *d-Glucose Sodium Chloride*, 2 $C_6H_{12}O_6$ + NaCl (two modifications)

$c = 10.46$, containing 0.90 $C_6H_{12}O_6$

First rotation after 15 minutes (for $C_6H_{12}O_6$)	+ 99.4°	Decrease 49.1°
Final rotation after 20 hours	+ 50.3°[3]	

5. *d-Glucoseoxime*, $C_6H_{12}O_5$.NOH (two modifications)

($c = 9.648$)

First rotation after 15 minutes	− 5.4°	Decrease 3.2°
Final rotation after 18 hours	− 2.2°[4]	

6. *d-Glucosephenylhydrazone*, $C_6H_{12}O_5.N_2H.C_6H_5$ (two modifications)

($c = 10$)

First rotation after 10 minutes	− 15.3°	Increase 31.6°
Final rotation after 12–15 hours	− 46.9°[5]	

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[1] Tanret: Compt. rend., **120**, 1060.
[2] Parcus and Tollens: Ann. Chem. (Liebig), **257**, 164.
[3] Trey: Ztschr. phys. Chem., **22**, 428.
[4] Jacobi: Ber. d. chem. Ges., **24**, 697.
[5] Jacobi: Ann. Chem. (Liebig), **272**, 173.

7. *l-Glucose*, $C_6H_{12}O_6$ (two modifications)

($c = 4\ 179$)

First rotation after 7 minutes	94.5°	Decrease
Final rotation after 7 hours	51.4°[1]	43.1°

8. *d-Galactose*, $C_6H_{12}O_6$ (three modifications)

α-Modification.—Ordinary crystallized galactose.

β-Modification.—This is obtained by dissolving the *α*-form in 1½ to 2 parts of boiling water and pouring the solution into eight times the volume of alcohol, stirring meanwhile, which produces a crystalline precipitate. The conversion of *α* into *β* is complete in strong solution only. It is soluble in 1.57 parts of water at 22°, and reverts into the *α*-form on crystallization from water.

The *γ-Modification* is said to be produced when a solution of 12 grams of *α*-galactose in 30 grams of water is treated with 0.03 gram of sodium phosphate and a drop of dilute sulphuric acid, warmed on the water-bath a few minutes, then cooled, and gradually mixed with 240 cc. of absolute alcohol. On repeating the process several times the rotation of the product, probably still impure, could be reduced to 52.25°. In aqueous solution at the ordinary temperature it is converted into *β* inside of two hours, while for conversion into *α* three times as long is required.[2]

Change of α into β

($c = 10$)

α First rotation after 7 minutes		117.4°	Decrease
β Final rotation after 6 hours		80.3°[3]	37.1°
α First rotation (Tanret)		135.0°	Decrease
β Final rotation "	85.3	81.6°	53.4

Change of γ into β.

γ First rotation after 5 minutes (Tanret)	52.3°	Increase
β Final rotation (Tanret)	81.6°	29.3°

9. *d-Galactoseoxime*, $C_6H_{12}O_5$ NOH (two modifications).

($c = 5.217$)

First rotation after 10 minutes	20.6°	Decrease
Final rotation after 20 hours	14.5°[4]	6.1°

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[1] E. Fischer Ber d chem Ges, **23**, 2619

[2] Tanret Bull Soc Chim, [3], **15**, 195

[3] Parcus and Tollens Ann Chem. (Liebig), **257**, 169

[4] Jacobi Ber d chem Ges, **24**, 698.

d-Mannoseoxime, $C_6H_{12}O_5.NOH$ (two modifications)

($c = 4.875$)

First rotation after 10 minutes	+ 7.5°	Decrease 4.3°
Final rotation after 6 hours	+ 3.2°[1]	

d-Fructose, Levulose, $C_6H_{12}O_6$

$c - 10, t = 20°$

First rotation after 6 minutes	— 104.0°	Decrease 11.7°
Final rotation after 20 to 25 minutes	— 92.3°[2]	
Final rotation	— 90.2°[3]	
Final rotation	— 90.7°[4]	

Rhamnose, *isodulcite*, $C_6H_{12}O_5$; *hydrate*, $C_6H_{14}O_6$ (three modifications)

α-Modification.—Ordinary rhamnose, crystallized from water. hydrate dissolved in water it shows a beginning rotation of 5° to — 7° (referred to $C_6H_{12}O_5$), then, by conversion into β-form, a decrease and afterwards a change to increasing ht rotation which reaches about + 10°.

β-Modification.—For the preparation of this 1 part of the orm is dissolved in ½ part of boiling water and then mixed h 5 parts of absolute alcohol and 5 parts of ether. The t crystalline precipitate which separates is α-rhamnose; is removed and a new portion of ether is added, which ows down the β-form, with which, however, a small amount the γ-form with lower rotation may be mixed. The β-form stallizes with ½ molecule of water in fine needles. It acts moisture from the air and reverts into the α-form. In eous solution it shows the constant right rotation of + 9.1° 0.1° or even 12 7°, referred to $C_6H_{12}O_5$[5]

-Modification—This is produced from the β-rhamnose n it is dried in a desiccator, and then heated for several rs to 90°. On crystallizing, it reverts to the α-form It ins with a rotation of + 22.8°, which gradually sinks to ut + 10° through conversion into the β-form.[6]

Jacobi· Ber. d chem. Ges., 24, 699.

Parcus and Tollens: Ann. Chem. (Liebig), 257, 166

Jungfleisch and Grimbert: Compt. rend., 107, 390

Hönig and Jesser. Wien. Akad., Ber., 97, II, 547.

Tanret: Bull. Soc. Chim., (3), 15, 202.

Tanret : *Loc. cit.*

Change of α into β.

Hydrate dissolved in water Calculated for $C_6H_{12}O_5$.

1 $c = 10$, $t = 20°$.

α	First rotation after 5.5 minutes	5°	Decrease and increase 14.4°
β	Final rotation after 66 minutes	+ 9.4°[1]	

2. $c = 9.08$, ordinary temperature.

α	First rotation after 1 minute	5.6°	Decrease and increase 14.8°
β	Final rotation after 1 hour	+ 9.2°[2]	

3. $c = 5$ and 10, t 13 5°.

α	First rotation after 10.5 minutes	7.1°	Decrease and increase 16.2°
β	Final rotation after 1 hour	+ 9.1°[3]	

Rhamnose anhydride dissolved in water (c 9.5) shows at once the constant rotation + 8.7 (β-form).[4]

Change of γ into β.

γ	First rotation	+ 22.8°	Decrease 12 7
β	Final rotation after 1 5 hours	+ 10.1°	

With alcohol as solvent different rotations are found. Jacobi (*loc cit.*) gives the following observations:

1 Hydrate, dissolved in alcohol, c 7.67.

First rotation, after 15 minutes (for $C_6H_{12}O_5$)	12.6°	Decrease 2 6
Final rotation after 16 hours " "	10.0°	

2 Anhydride dissolved in alcohol, c 7.5.

First rotation after 5 minutes (for $C_6H_{12}O_5$)	3 4°	Decrease and increase 12 4
Final rotation after 24 hours " "	9.0°	

For the explanation of the phenomenon that the hydrate and anhydride of rhamnose show a rotation in alcohol opposed to that in water see § 64.

13. *Rhamnoseoxime*, $C_6H_{12}O_4.NOH$ (two modifications)

$c = 9$ 863, ordinary temperature

First rotation after 10 minutes	+ 6.1°	Increase 7.5°
Final rotation after 20 hours	+ 13.6°[5]	

14. *Fucose*, $C_6H_{12}O_5$ (two modifications)

$c = 6.916$, $t = 20°$.

First rotation after 11 minutes	− 111.8°	Decrease 34.8°
Final rotation after 2 hours	− 77.0°[6]	

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[1] Schnelle and Tollens · Ann. Chem. (Liebig), **271**, 63.

[2] Jacobi · Ann Chem (Liebig), **272**, 176.

[3] Tanret *Loc cit*

[4] Jacobi Ann Chem (Liebig), **272**, 177

[5] Jacobi Ber. d chem. Ges , **24**, 698.

[6] Gunther and Tollens Ann Chem (Liebig), **271**, 90.

Rhamnohexose, $C_7H_{14}O_6$ (two modifications)

c 10, t 20°.

irst rotation after ½ hour	$-$ 82.9°	Decrease 21.5°
inal rotation after 12 hours	$-$ 61.4°[1]	

d-Mannoheptose, $C_7H_{14}O_7$ (two modifications)

c 10.14 ordinary temperature.

irst rotation after 10 minutes	+ 85.1°	Decrease 16.5°
inal rotation after 24 hours	+ 68.6°[2]	

α-Glucoheptose, $C_7H_{14}O_7$ (two modifications)

c 10, t 20 .

irst rotation after 15 minutes	- 25.0°	Decrease 5.3°
inal rotation after some hours......	- 19.7°[3]	

α-Glucooctose, $C_8H_{16}O_8$ + 2 H_2O (two modifications)

c 6.637, dissolved at 50° and cooled

irst rotation	- 61.4°	Decrease 17.5°
inal rotation after 6 hours.	43.9°[4]	

Milk-sugar, $C_{12}H_{22}O_{11}$ (three modifications)

Modification.—Ordinary crystallized milk-sugar, $C_{12}H_{22}O_{11}$ + This exhibits a beginning rotation of + 87° (anhydrous) n aqueous solution is changed into the β-form.[5]

Modification This may be obtained from α and β, and is ed in crystalline form, $C_{12}H_{22}O_{11}$ + 1/2 H_2O, by adding or four volumes of absolute alcohol to the warm concen- l solution of either of these.[6]

e γ-form is obtained by rapidly evaporating a solution of r three grams of α-milk-sugar in 10 cc. of water to dry- n a platinum-dish on a water-bath, and drying the resi- t 98° to complete loss of the water of crystallization.[7] y also be obtained by rapidly boiling down a solution of ary milk-sugar in a metallic vessel, when suddenly the : liquid solidifies to a mass of small porous anhydrous ls.[8] Pure anhydrous crystals may be secured by repeated

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scher and Piloty: Ber. d. chem. Ges., 23, 3102

scher and Passmore. Ber. d. chem. Ges., 23, 2230.

scher: Ann. Chem. (Liebig), 270, 75.

scher Ann. Chem. (Liebig), 270, 97.

rdmann and Schmöger. Ber. d. chem. Ges., 13, 1922.

inret: Bull. Soc. Chim., (3), 13, 625.

hmöger Ber. d. chem. Ges., 13, 1915.

rdmann Ber. d. chem. Ges., 13, 2180.

crystallization from anhydrous alcohol (Tanret). The first rotation is + 36.2°, which increases to that of the β-form.

The three forms show the same freezing-point depression.

If ordinary powdered milk-sugar is dehydrated at 130°, the residue shows the rotation phenomena of the α-form.

Change of α into β

1. $c = 7.5$ (hydrate), $t = 20°$.

	Calculated for $C_{12}H_{24}O_{12}$.	$C_{12}H_{22}O_{11}$.	
α First rotation after 4 minutes..	84.0	88.4°	Decrease
β Final rotation after 6 hours....	52.5	55.3°[1]	33.1°

2. $c = 4\,841$ (hydrate). t 20°

α First rotation after 8 minutes.	82.9°	87.3°	Decrease
β Final rotation after 24 hours..	52.5	55.3°[2]	32.0°

Change of γ into β.

$c = 7\,07, 7\,72$; ordinary temperature.

γ First rotation................	34.4°	36.2°	Increase
β Final rotation after 24 hours...	52.45	55.2°[3]	19.0°

20. *Maltose*, $C_{12}H_{22}O_{11}$ (two modifications); hydrate,

$$C_{12}H_{22}O_{11} + H_2O$$

1. $c = 14$ to 19 (anhydride) t - 15°.

	for $C_{12}H_{22}O_{11}$.	
First rotation after 4 minutes. .	122.0 to 124.8°	Increase
Final rotation after 12 hours.....	.... 138.3°[4]	13.5°

2 $c = 9.2$ to 9 8 (anhydride), t - 20°.

First rotation after 6 to 12 minutes	118.8 to 121.0°	Increase
Final rotation after 5 to 9 hours	136.8 to 137.0°[5]	17.0°

The absence of multirotation has been shown for inosite, sorbin, levosin, ethyl glucoside, methyl and ethyl galactosides, benzyl arabinoside, and the phenyl hydrazones of galactose and rhamnose.

73. Rate of Change in Rotation.—Urech[6] was the first to show that the Wilhelmy velocity formula for reactions of the first order,

$$\frac{dx}{dt} = C\,(A - x),$$

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[1] Schmöger Ber. d. chem Ges, **13**, 1931.

[2] Parcus and Tollens Ann. Chem (Liebig), **257**, 170.

[3] Schmöger Ber. d chem Ges., **13**, 1918.

[4] Meissl J prakt Chem., (2) **25**, 122.

[5] Parcus and Tollens. Ann Chem. (Liebig), **257**, 172.

[6] Urech Ber. d chem Ges, **16**, II, 2270 (1883); **17**, I, 1547; **18**, II, 3059.

applicable to the case of the change of rotation in milk-sugar
d grape-sugar. New and careful investigations with refer-
ce to dextrose have been carried out by Levy[1] and by
ey.[2] In consideration of the fact that the actual beginning
ation is a quantity which can never be accurately deter-
ned here, the first of these observers changed the formula
ed in calculating the constant, C,

$$\text{I} \qquad C = \frac{1}{t} \cdot \log\left(\frac{A}{A - x}\right)$$

$$\text{II} \qquad C = \frac{1}{t_2 - t_1} \cdot \log\left(\frac{\beta_1 - \varphi}{\beta_2 - \varphi}\right),$$

which $\beta_1 \beta_2$ are the rotations corresponding to the times $t_1 t_2$,
φ represents the constant final rotation.[3]
n illustration the following series of observations by Levy
be given

FOR A SOLUTION OF ANHYDROUS DEXTROSE OF 3.502 PER CENT STRENGTH d_4^{20} = 1.0114. TEMPERATURE, 20.5° TO 20.9°.

me in minutes after solution		Observed angle of rotation 2 dm		$t_2 - t_1$	Temperature	Constant C, formula II.
t	25	β_1	27.865°	0	20.9°	
t	30	β	27.060	5	20.9	0.00649
t	35	β_2	26.159	10	20.9	0.00719
t_2	40	β_2	25.637	15	20.8	0.00644
t_2	45	β_2	24.927	20	20.7	0.00662
t_2	50	β_2	24.369	25	20.6	0.00652
t	55	β	23.895	30	20.5	0.00636
t_2	60	β_2	23.166	35	20.5	0.00677
t_2	65	β_2	22.797	40	20.5	0.00656
t_2	70	β_2	22.171	45	20.5	0.00687
t_2	75	β_2	21.837	50	20.5	0.00674
t_2	80	β_2	21.470	55	20.5	0.00671
t_2	85	β_2	21.088	60	20.5	0.00675
24 hours		φ	16.692		Mean	0.00662

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[1] evy: Ztschr. phys. Chem., 17, 301 (1895).

[2] rey: Ibid., 18, 193; 22, 484.

[3] he same formula was derived somewhat earlier by P. Th. Müller: Compt. rend.,

From fifteen series of experiments made at a nearly constant temperature of 20°, Levy found that for strengths of 1 to 5 per cent., the constant, C, is independent of the concentration. With increasing temperature, the value increases. It was found in the mean, that for

$$\text{about } 20.10^\circ \quad C = 0.00610$$
$$20.25^\circ \quad C = 0.00637.$$

Effect of Added Substances on the Velocity of Transformation

The decrease in the rotation of aqueous dextrose solutions with the time, is sometimes hastened and sometimes retarded by the presence of other substances, such as acids, alkalies or salts, and the behavior of these bodies appears to be a catalytic one. Numerous investigations by Levy and Trey have shown the following facts.

a. Bodies Which Hasten the Change

1 Acids.—The effect of these was first noticed by Erdmann[1] in the case of milk-sugar. According to Levy,[2] the velocity constant, C, (formula II) assumes the following values when dilute acids containing $\frac{1}{10}$ mol. to the liter were employed as solvents

	C	Temperature	Relative acceleration
Water	0.00610	20.1	.
Water	0.00637	20.25	.
Hydrochloric acid	0.02300	20.25	100
Nitric acid	0.02283	20.1	98.99
Trichloracetic acid	0.02325	20.25	96.67
Sulphuric acid	0.01886	20.0	71.95
Dichloracetic acid	0.01670	20.2	62.41
Monochloracetic acid	0.01004	20.25	17.25
Acetic acid	0.00716	20.2	4.70
Propionic acid	0.00636	19.8	1.63

It appears, therefore, that in their accelerating behavior, the acids stand in the order of their affinity coefficients, as measured by electrical conductivity, the catalysis of methyl acetate or by their power of inverting cane-sugar.

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[1] Erdmann Jahresber., 1855, p. 671

[2] Levy *Loc. cit.*, p. 301

Trey[1] came to the same conclusion in experiments on the action of hydrochloric, sulphuric, oxalic, and cacodylic acids. But, on the other hand, he found a retarding effect with acetic and propionic acids.

The value of the constant, C, increases as a matter of course, with the strength of the acid. For example, with $\frac{1}{50}$ normal hydrochloric acid, the value is $C = 0.00971$.

2. *Bases.*—These bring about an enormous acceleration in the velocity of transformation of all sugars, so that in a very few minutes, or immediately after the addition of the base, the normal end rotation is reached. This was first noticed by Urech[2] in the case of milk-sugar and ammonia, and he found also that in time, the rotation sinks still lower, which may be accounted for by a chemical change in the sugar.[3]

The action of ammonia on different sugars has been thoroughly investigated by Schulze and Tollens.[4] They found that by application of 0.1 per cent ammonia, after 5 to 10 minutes, even, the normal lower rotation is reached with dextrose, xylose, arabinose, galactose, rhamnose, levulose, and ordinary milk-sugar. This was found to be the case with γ-milk-sugar and maltose also, from which it is seen that not only the higher, but the lower rotation as well, is destroyed immediately. Schulze and Tollens observed, for example, the following changes

Xylose		$[\alpha]_D$	Maltose hydrate		$[\alpha]_D$
In water constant		$+18.7°$	In water constant		$+130°$
In ammonia of 20.4 per cent. d 0.924	After 10 min.	$+14.8$	In ammonia of 20.4 per cent.	After 10 min	$+126.1$
	After 1 day	$+11.0$		After $7\frac{1}{2}$ hours	$+123.9$
	After 3 days	$+5.7$		After 1 day	$+118.1$
	After 5 days	-5.9			

In the same manner Trey[5] found in a solution, which contained in 100 cc., 2.25 grams of dextrose anhydride and 0.085 NH_3,

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[1] Trey: Ztschr. phys. Chem., 18, 205; 22, 448.

[2] Urech: Ber. d. chem. Ges., 15, 2132 (1882).

[3] Urech: *Ibid.*, 17, 1545.

[4] Schulze and Tollens: Ann. Chem. (Liebig), 271, 49.

[5] Trey: Ztschr. phys. Chem., 22, 439.

After 15 min.	$[\alpha]_D$	52.2 (normal)
After 24 hours		49.6
After 65 days		44.9

The alkali hydroxides have an equally strong action; by means of $\frac{1}{200}$ normal potassium hydroxide solution the final rotation in dextrose is reached almost instantly. With greater concentration, a further progressive decrease is observed which may even pass into left rotation. Thus, Trey[1] found in a solution containing in 100 cc. 2.25 grams of dextrose, and 0.3 gram of sodium hydroxide, the following specific rotations

After 15 minutes	$[\alpha]_D$	52.7 (normal)
" 24 hours	$[\alpha]_D$	36.7
" 48 "	$[\alpha]_D$	26.0
" 34 days	$[\alpha]_D$	15.1
" 65 "	$[\alpha]_D$	0.4

It is evident that some chemical change takes place here As Lobry de Bruyn and Alberda van Ekenstein[2] have observed, the reciprocal conversion of dextrose, levulose, and mannose into each other by the catalytic action of small amounts of alkali is possible.

It is only with very weak bases that the fall in the multirotation may be quantitatively followed. This was done in a dextrose solution containing urea with which Levy[3] found the following values for the velocity constant, C (formula II)

Urea in solution { 10 per cent. : C 0.00833 at about 20°
5 per cent. : C 0.00749 at about 20°

These numbers are but little larger than given above for pure water.

3 *Salts.*—These all, with the exception of sodium chloride, have an accelerating action on the fall of rotation in dextrose.

Salts with an alkaline reaction bring about the normal end rotation within a few minutes. This is the case with sodium carbonate, with which, after long standing, no further decrease is observed; this salt is therefore suitable for quickly destroying the multirotation. Potassium cyanide sometimes produces a marked decrease below the normal end value (Trey).[4]

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[1] Trey · *Loc. cit.*, p. 438.

[2] Lobry de Bruyn and Alberda van Eckenstein: Ber. d. chem. Ges., 28, III, 3078; Rec trav. chim. Pays-Bas., 14, 156, 203.

[3] Levy: Ztschr. phys. Chem., 17, 324.

[4] Trey: *Ibid.*, 22, 440.

Salts with a neutral reaction cause a slower decrease in the ultirotation, so that the conversion may be followed and meas- ed. Levy[1] found the velocity constant *C* (formula II), for xtrose in the presence of the following salts:

	C	Temp.
Pure water	0.00610	20.1°
Sodium sulphate, anhydrous, 10 per cent	0.00844	20.0
Sodium sulphate, anhydrous, 5 per cent	0.00800	20.2
Sodium acetate, 10 per cent	0.03897	20.1

According to Levy, the action of these salts depend on this, at through partial hydrolysis, sodium hydroxide is formed hich brings about the acceleration This hydrolysis takes ace to a greater extent with sodium acetate, than with the lphate, and this explains its much stronger effect

Trey has demonstrated the accelerating action of the follow- g salts on the fall of rotation in dextrose[2]

Sodium bicarbonate,
Potassium nitrate
Potassium iodide,
Ammonium chloride,
Ammonium thiocyanate,
Barium chloride,
Magnesium chloride,
Magnesium sulphate,
Aluminum chloride,
Cadmium iodide,
Lead acetate,
Mercuric chloride.

Trey found also that sodium sulphate lessens the effect of lphuric acid

b. Bodies Which Retard the Change

1 *Sodium Chloride*.—The behavior of this salt, different m that of all others, was first noticed by Levy[3] who found following values for the constant *C* (by formula II), ich are smaller than that for water:

Dextrose solution	*C*	Temp.
In pure water	0.00610	20.1°
In 10 per cent. sodium chloride	0.00533	20.0
In 5 per cent. sodium chloride	0.00586	20.2

Trey[4] confirmed this retarding action of common salt by following series of observations, in which the changes in specific rotation of dextrose with the time of standing were nd:

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[1] Levy: *Loc. cit.*

[2] Trey: Ztschr. phys. Chem., **22**, 429.

[3] Levy. *Ibid.*, **17**, 320.

[4] Trey. *Ibid.*, **22**, 429, 436.

Dextrose	2.250		9.000			
NaCl	0	0.2925	0	0.2925	0.585	1.170
me, 5 min	102.7°	.	100.0°	..	..	..
me, 15 min	95.6	96.0°	94.2	96.8°	97.3°	97.1°
me, 25 min.	87.3	90.0	86.4	89.6	89.9	89.7
me, 35 min.	82.2	84.4	80.2	83.2	83.7	83.3
me, 45 min.	78.2	80.4	74.6	77.9	78.5	78.1
me, 55 min	74.4	76.7	69.9	73.1	73.2	73.6
me, 65 min	72.2	74.9	66.2	69.4	69.6	70.7
me, ∞	50.7°	51.1°	50.8°	51.1°	51.7°	52.2°

In presence of common salt the decrease in the rotation ollows more slowly than in pure water. It is seen also that a ariation in the amount of salt is of little importance. An xplanation of this peculiar behavior of the salt is wholly acking

2 *Alcohols and Other Organic Substances.*—Levy obtained, ccording to formula II, lower values for the constant, C, with solutions of dextrose in aqueous ethyl alcohol than in pure water.

		C	Temp
Pure water		0.00610	20.1°
In 1 liter	$^1/_{10}$ mol. alcohol	0.00555	20.0
	$^1/_5$ mol alcohol	0.00521	20.0
	1 mol. alcohol	0.00510	20.1

In aqueous methyl alcohol, the retarding action of which had been already observed by Dubrunfaut,[1] Trey[2] found that the decrease in the rotation takes place somewhat more rapidly than in ethyl alcohol.

Solutions of dextrose in pure methyl alcohol show likewise, multirotation, and the decrease in the same may be retarded by addition of other organic substances. Trey[3] found the velocity constant from formula I for the following solutions ·

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[1] Dubrunfaut Compt. rend., **42**, 228 (1856)

[2] Trey Ztschr phys Chem, **17**, 200

[3] Trey *Ibid*, **17**, 200

In 100 cc of the methyl alcohol solution	C
1.0775 gram dextrose	4.95
1.0210 " " + 0.1525 gram phenol	2.54
0 9615 " " + 0.1543 " naphthalene	1.77
0.8504 " " + 0 2725 " diphenylamine	1.11
0 8495 " " + 0 3072 " succinamide	0 85

Finally, a retardation in the decrease in rotation in aqueous lextrose solutions has been noticed on addition of acetone and lso of cane-sugar (Trey)[1]

74. **Cause of Multirotation of the Sugars.**—On this point, the ollowing views have been advanced ·

1 The change in the rotation may depend on this, that in he original freshly prepared solution, molecular aggregations crystal molecules) of active form may exist, which gradually reak down into molecules of lower rotation (Landolt,[2] ribram,[3] Hammerschmidt,[4] Wyrouboff)[5]

By cryoscopic methods, as already explained in § 63, these ggregations cannot be shown, because they no longer exist n dilute solutions

2 With dextrose, which shows multirotation as an anhyride as well as hydrate, the fall in rotation may be due to the aking up, or splitting off, of water. This view which was rought forward years ago by Erdmann[6] and Béchamp,[7] and ater abandoned by its authors has recently come to light again Fischer[8] is of the opinion that anhydrous grape-sugar disolves first as $C_6H_{12}O_6$ (with high rotation) and is gradually ransformed into the hydrate or heptahydric alcohol, $C_6H_{14}O_7$ with lower rotation) According to Jacobi,[9] this view is onfirmed by the fact, that in birotating glucose anhydride olutions, the formation of the phenyl hydrazone takes place nore rapidly than in the lower rotating solutions On the

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[1] Trey Ztschr phys Chem, **22**, 450, 456

[2] Landolt "Optisches Drehungsvermögen," 1st ed (1879), p 58

[3] Pribram Wien Monatsheft, **9**, 401

[4] Hammerschmidt: Ztschr f Rübenzucker-Ind, **40**, 939

[5] Wyrouboff Compt rend, **115**, 832

[6] Erdmann Jahresbericht, (1855), p 672

[7] Béchamp *Ibid*, (1856), p. 639, 640, Compt rend, **42**, 640, 896

[8] E Fischer · Ber d chem Ges, **23**, 2626

[9] Jacobi Ann Chem (Liebig), **272**, 179

other hand, Tollens[1] assumed that the anhydride on dissolving is transformed immediately into the hydrate (with high rotation), as evolution of heat follows, and that then gradually, in solution, a reformation of the anhydride (with low rotation) takes place. Such a reaction is, however, thermodynamically impossible. With dextrose hydrate, which dissolves without liberation of heat, the high rotation of the unchanged compound which at first appears, and the decrease in the rotation, would both have to be ascribed to the gradual formation of anhydride.

Arrhenius,[2] and also Brown and Morris[3] have found that birotating and normally rotating dextrose solutions are cryoscopically identical. But this observation does not decide the question as to the presence of hydrate or anhydride in solution because the difference between the freezing point depressions of the two would be so small as to fall within the limits of errors of experiment.

3 The differences in rotation of multirotating sugars may be due to the existence of different isomeric modifications which, in solution, are gradually transformed into each other.

Such an assumption was made as early as 1856 by Erdmann,[4] Dubrunfaut,[5] and also by Béchamp,[6] and with the understanding that of the different modifications, one is crystalline and the others amorphous. But since then, as explained in §§ 71 and 72, Tanret has succeeded in obtaining the two or three different rotating forms of several sugars in crystalline condition, and in showing the equality in their molecular weights, and also their reciprocal convertibility. There remains, therefore, only the question as to the constitution of these isomers, and on this point van't Hoff[7] called attention (1894) to the clue which may be found in the analogy existing between the sugars and the rotating lactone-forming acids, as gluconic acid, arabonic acid, saccharic acid, and others. With

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[1] Tollens Ber. d. chem. Ges., 26, 1799.

[2] Arrhenius; Ztschr phys. Chem., 2, 500 (1888).

[3] Brown and Morris: Chem. News, 57, 196 (1888).

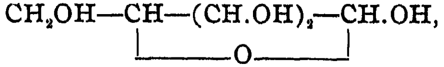
[4] Erdmann · Jahresbericht, (1855), 672; (1856), 639: Ber d. chem. Ges., 13, 2180 (1880)

[5] Dubrunfaut: Compt. rend., 42, 739 (1856).

[6] Béchamp: Compt. rend., 42, 896 (1856); Bull. Soc. Chim., (3), 9, 511 (1893).

[7] van't Hoff "Lagerung der Atome im Raume," 2d ed., p. 111.

:se latter, as will be explained in § 75, the increase in rota-
n, which follows on solution in water, depends on the
mation of their lactones, which possess a cyclic constitution.
ı the other hand, a decrease in rotation results when the
tones are changed into the acids, with destruction of the
g formation. According to this, for example, of the two
difications of xylose the higher rotating might have the
mula



$$CH_2OH—CH—(CH.OH)_2—CH.OH,$$

1 the change into the lower rotating form might depend on
: conversion into a body of this structure,

$$CH_2OH—(CH\ OH)_3—CHO.$$

Further, it was observed simultaneously by E von Lipp-
nn[1] and by Lobry de Bruyn and Alberda van Ekenstein[2]
ıt in regard to the three differently rotating *d*-glucoses, the
umption of the ethylene oxide constitution of the same pro-
les for two stereoisomeric forms, and that the third or
ehyde structure may also appear

While it is true that the proof of which constitution must
ascribed to each of the three forms of glucose, etc , is as
a very difficult question, we may now consider this much
established, that the cause of the multirotation in the sugars
to be found in the transformations of their different isomeric
difications.[3]

II. Multirotation of Oxy-Acids and Their Lactones.

'5. In 1873 Wislicenus[4] made the observation that the
ating power of *d*-lactic acid, in aqueous solution, is gradu-
y changed at the ordinary temperature, and he found the
ise of this to lie in the slow hydration of anhydrous mole-
es which were contained in the solution. The same behavior
s later noticed, especially by Tollens, in other oxy-acids, as
charic acid, gluconic acid, rhamnonic acid and others, and

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[1] E. v. Lippmann: Ber. d. chem. Ges., 29, 203, "Chemie der Zuckerarten," (1895), 30, 990, 992.

[2] Lobry de Bruyn and Alberda van Ekenstein. Ber d. chem Ges., 28, 3081 (1895).

[3] See a recent paper by Brown and Pickering (J. Chem Soc., 71, 769) on this lect

[4] Wislicenus: Ann. Chem. (Liebig), 167, 302.

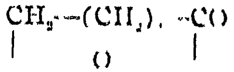
also in their lactones. The latter have always a markedly greater rotation than the corresponding acids, and if the lactones are dissolved in water there is found a progressive decrease in the rotation until a constant value is finally reached If, on the other hand, fresh solutions of the acids are made by using salts of the same and hydrochloric acid in addition, then a gradual fall of the rotation may be observed, and finally the same value is reached as is obtained by starting with the lactone.

The cause of the phenomenon is found in this fact, that in aqueous solution, both the acid and its lactone suffer a reciprocal decomposition which goes on very slowly and continues until a condition of equilibrium is reached when the liquid contains both substances in definite proportions. This ratio varies with the temperature, and in such a manner that with elevation of temperature there is an increase of the lactone molecules, and therefore of the rotation. On cooling, the rotation decreases to its former value.

The velocity relations in the conversion of the oxy-salts into their lactones, and the reverse, have been studied especially by P Henry[1] who made use of

γ-oxybutyric acid and lactone

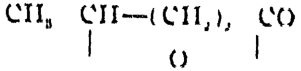
$CH_2OH—(CH_2)_2—COOH$



$\underset{|\qquad O \qquad|}{CH_2—(CH_2)_2—CO}$

γ-oxyvaleric acid and lactone

$CH_3—CH.OH—(CH_2)_2—COOH$



$CH_3\ \underset{|\qquad O \qquad|}{CH—(CH_2)_2\ CO}$

in which case by titrations the following relations were found:

a. The transformation of the oxy-acids into lactones is hastened by addition of acids, which act catalytically. The velocity is expressed by the equation corresponding to a reaction of the first order,

$$\frac{dx}{dt} = C(A-x),$$

in which A represents the original amount of oxy-acid, x the amount of lactone formed in the time, t, and C the constant of the reaction. It was found that different acids added act with an intensity proportional to their affinity coefficients. γ-Oxybutyric acid is transformed only partially, but with γ-oxyvaleric acid the reaction is complete.

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[1] P. Henry Ztschr phys. Chem., 10, 96 (1892). See also: K. Hjelt. Ber. d. chem. Ges, 24, 1236 (1891); Unno Collan: Ztschr. phys. Chem., 10, 130 (1892).

b. In the case of spontaneous transformation of the oxy-acids into lactones, the relations observed correspond to the assumption that the oxy-acid still remaining, at any moment, can accelerate its own conversion; that is, autocatalysis comes into play. The above formula no longer holds good, since in this case the velocity of the reaction is proportional to the amount of acid not dissociated, that is to $C(A-x)$, considered as an indifferent body, and also to the dissociated, catalytically acting acid, which at any moment is equal to $y(A-x)$, where y is a certain function which expresses the number of H-ions The complete expression for the velocity is given then by the equation obtaining for a reaction of the second order,

$$\frac{dx}{dt} = Cy(A-x)^2,$$

which was found to give values for C in accord with the results of experiment For the derivation of y the original paper must be consulted.[1]

c Addition of bases to the solution of the lactone hastens the conversion of the latter into acid When the two bodies are mixed in equivalent proportions the velocity of the reaction corresponds to the equation,

$$\frac{dx}{dt} = C(A-x)^2$$

It was found that the activity of the bases is proportional to the intensity of their basic character

Observations.—On the multirotation of oxy-acids and lactones the most important results are, in the main, the following, and among these, those concerning saccharic acid are given first, because here the condition of equilibrium referred to above is most clearly discerned (c = concentration in 100 cc.).[2]

---

[1] See also H. Jahn: "Grundriss der Electrochemie," (1895), p 118.

[2] In the calculation of the specific rotation of the several solutions, which contain acid and lactone at the same time, it is necessary to express the concentration in terms of either one or the other In each case it is stated to which bodies the numbers given refer.

1. *d-Saccharic acid*,[1] $C_6H_{10}O_8$.

Acid ammonium salt with HCl.
$c = 4.634$ acid $= 4.237$ lactone

	$[\alpha]_D$
Beginning	+ 9.1°
After 1 day	11.0
" 2 days	13.2
" 4 "	15.5
" 5 "	16.4
" 6 "	17.2
" 8 "	18.5
" 12 "	20.5
" 14 "	20.8
" 29 "	22.7

Calculated for $C_6H_8O_7$

Saccharic acid lactone, $C_6H_8O_7$.

Weighed directly
$c = 10.213$ lactone

	$[\alpha]_D$
Beginning	+ 37.9°
After 4 days	32.3
" 6 "	30.5
" 11 "	26.3
" 13 "	24.9
" 17 "	24.1
" 24 "	23.2
" 27 "	23.1
" 31 "	22.9
" 35 "	22.9
" 39 "	22.8
" 56 "	22.5

Calculated for $C_6H_8O_7$.

With norisosaccharic acid, $C_6H_{10}O_8$, and isosaccharic acid, $C_6H_8O_7$, almost the same rotation is likewise found after warming the solutions (+49 to + 52).[2]

2. *Rhamnonic acid*, $C_6H_{12}O_6$

Strontium salt and HCl
$c = 6.204$ acid

	$[\alpha]_D$
After 10 minutes	— 7.7°
" 18 "	11.1
" 33 "	15.8
" 2 hours	27.9
" 3½ "	29.3
" 3 days	29.4
" 5 "	29.2
Heated ½ hour at 100° and cooled	34.3
After 1 day	30.7
" 3 days	30.1
" 5 "	30.1

Calculated for $C_6H_{12}O_6$

Rhamnonic acid lactone $C_6H_{10}O_5$.

Weighed directly
$c = 5.680$ lactone $= 5.960$ acid

	$[\alpha]_D$
At once	— 34.3°
After 1 day	34.3
" 2 days	33.7
" 3 "	33.7
" ½ hour heated	34.8
" 3 days	34.0

Calculated for $C_6H_{12}O_6$.

It appears, therefore, that in the condition of equilibrium the liquid contains mainly the lactone, and that probably the latter is not transformed into the acid at all.[3]

[1] Sohst and Tollens Ann Chem (Liebig), 245, 10, 12

[2] Tiemann: Ber d chem Ges, 27, 137

[3] Schnelle and Tollens: Ann. Chem. (Liebig), 271, 72

3. *d-Gluconic acid*,[1]
$C_6H_{12}O_7$.
Calcium salt with oxalic acid.

	$[\alpha]_D$
At the beginning	− 1.74°
After 14 to 21 days	+ 10 to 12
Heated to 100°	+ 23.4
After cooling	+ 10 to 12

Calculated for $C_6H_{12}O_7$

Gluconic acid lactone,
$C_6H_{10}O_6$.
c = 7.5 lactone

	$[\alpha]_D$
After 10 minutes	+ 55.9°
" 1 day	+ 47.6
" 3 days	+ 44.0
" 8 days	+ 36.0
" 11 days	+ 33.6
" 47 days	+ 18.9

Calculated for $C_6H_{12}O_7$.

The conversion of the lactone into the acid takes place, therefore, very slowly and after forty-seven days is not yet complete. It may be further remarked, as with rhamnonic acid, that heating the acid leads to increased formation of lactone.

4. *d-Galactonic acid*,[2]
$C_6H_{12}O_7$
Calcium salt with HCl
c = 7.52 acid

	$[\alpha]_D$
After 10 to 15 min	− 10.6°
" 5 hours	13.8
" 6 days	39.2
" 15 days	45.9
Heated to 100°	59.7
After 14 days	53.0

Calculated for $C_6H_{12}O_7$.

Galactonic acid lactone,
$C_6H_{10}O_6$.
Weighed as hydrate
$C_6H_{10}O_6 + H_2O$ c = 6.85

	$[\alpha]_D$
After 10 min	− 64.2°
" 24 hours	63.7
" warming	− 63.9
2 c = 7.0	
After 10 min	− 65.5
" 3 days	− 64.3

Calculated for $C_6H_{12}O_7$

With many bodies, the following for example, the observations are still incomplete

5. *Arabonic acid*,[3]
$C_5H_{10}O_6$.
Strontium salt and HCl.
c = 3.46 acid

	$[\alpha]_D$
After 10 min	− 8.50°
" 4 hours	− 30.0
" 6 hours	37.0
" 20 hours	45.0
" 2 days	− 45.9
" 2 months	− 48.2

Calculated for $C_5H_{10}O_6$.

Arabonic acid lactone,[4]
$C_5H_8O_5$.
Weighed directly
c = 9.749 lactone

	$[\alpha]_D$
Beginning	− 65.9°
After 14 hours	− 65.9

Calculated for $C_5H_{10}O_6$.
(− 73.9 calculated for $C_5H_8O_5$.)

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[1] Schnelle and Tollens: Ann. Chem. (Liebig), **271**, 74.

[2] Schnelle and Tollens. *Ibid.*, **271**, 81.

[3] Allen and Tollens: *Ibid.*, **260**, 312.

[4] Fischer and Piloty: Ber. d. chem. Ges., **24**, 4219.

6. *Xylonic acid,*[1] $C_5H_{10}O_6$. *Xylonic acid lactone* $C_5H_8O_5$

Observations on the acid only have been made
Strontium salt and HCl. $c = 3\ 428$ $C_5H_{10}O_6$

After	10 min.	4 hours	6 hours	20 hours	later	2 months
[α]	− 7 1	0	+ 7 1	+ 17.2	+ 17.5	+ 20.9°.

7. *Saccharinic acid,* $C_6H_{12}O_6$. *Saccharin,* $C_6H_{10}O_5$.

For saccharin ($c = 10\ 4$) there was found:

After	8 min.	3 days	4 days	7 days	11 days
[α]	− 94.2	+ 90.7	+ 90 5	+ 88 9	+ 88.7°.

The changes in the rotation of saccharinic acid (salts of the acid with HCl) have not yet been investigated.

Isosaccharin ($c = 10$, $[\alpha]_D = + 63°$) and metasaccharin ($c = 10$, $[\alpha]_D = - 46.7°$) show constant rotation.[2]

8 *β-Glucoheptonic acid lactone,*[3] $C_7H_{12}O_7$

$c = 10\ 422$

after	20 min.	24 hours
$[\alpha]_D =$	− 79 2	− 67 7°.

9 *Anhydrides of d-Lactic Acid,* $C_3H_6O_3$.

As Wislicenus has shown, the right-rotating acid leaves on concentration, products which contain certain amounts of the strongly left-rotating anhydride, $C_6H_{10}O_5$, and probably the lactide, $C_6H_8O_4$ These last, when brought into aqueous solution, pass gradually back into lactic acid, which may be recognized by the fact that after neutralization the liquid becomes slowly acid. In consequence of this, the rotation increases, but at the ordinary temperature, this increase is appreciable only after some months

If, after standing some time, the solution be diluted with water, this produces at first a decrease in the rotation, and then later a gradual increase. According to Wislicenus, the decrease depends on the formation of a hydrate, $C_3H_6O_3 . H_2O$, whose rotation must be smaller than that of the acid

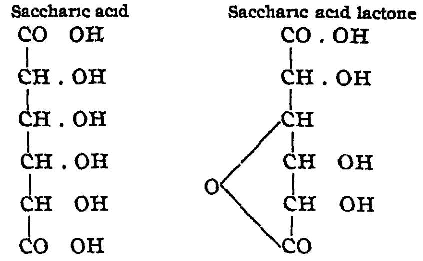
Among the experiments which Wislicenus[4] has made, the following may be cited:

---

[1] Allen and Tollens Ann. Chem (Liebig), **260**, 311
[2] Schnelle and Tollens *Ibid*, **271**, 66
[3] Fischer. *Ibid*, **270**, 85
[4] Wislicenus *Ibid*, **167**, 324 (1873), also **164**, 181

	$C_3H_6O_3$ in 100 cc	$[\alpha]_D$
Beginning	42.65	+ 0.41°
After 7 months	42 97	+ 2.85
" 9 "	42.97	+ 2.91
" dilution	15.74	+ 1.43
" 44 days	15.74	+ 1.84

Among bodies of Class II it is found, without exception, that the lactones possess a much stronger rotating power than their corresponding acids In the constitution of the two groups, there is a marked difference, as we have for example:



The higher rotation of the lactone may be attributed to the ring structure contained in it See § 84

Furthermore, it has not been shown in all cases that the decrease in rotation, which is observed with the lactones, depends on hydration. In the case of the β-glucoheptonic acid lactone, referred to above, Fischer was unable to discover any gradual formation of acid Besides, the change in rotation may take place in solutions which are not aqueous This was first observed by Colson[1] with the anhydride of diacetyl tartaric acid, which showed at first, in acetone, a rotation of + 12°, and after half an hour only + 10 18°

III Multirotation of a Few Other Substances

76. Here we have the following bodies

Formylfenchylamine, $C_{10}H_{17}$ NH.HCO —A solution in chloroform showed a decrease in rotation which ceased after 12 hours.[2]

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[1] Colson Bull Soc Chim, (3) 7, 805

[2] Binz Ztschr phys Chem, 12, 726

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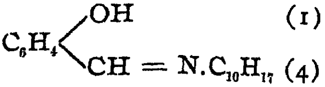
p-Oxy-benzylidenefenchylamine, 

$$C_6H_4 \begin{cases} OH & (1) \\ CH = N.C_{10}H_{17} & (4) \end{cases}$$

With a solution in chloroform ($p = 1.28$, $d = 1.4905$) there was found:[1]

For the fresh solution .... $[\alpha]^{20}_{D} = +77°$
After 18 hours .... $[\alpha]^{20}_{D} = +72$

Nicotine, dissolved in water.—Pribram observed that a solution of 20.169 per cent. strength, with a density of 1.0149, when allowed to remain in the polarization tube at the ordinary temperature, exhibited the following increase in rotation:

	$[\alpha]^{20}_{D}$ for $l = 3.999$ dm	$[\alpha]^{20}_{D}$
Fresh solution	— 7.188°	— 87.81°
After 12 hours	7.623	93.13
After 18 hours.........	7.903	96.55
After 48 hours	7.904	96.56

According to Pribram, this phenomenon depends on the formation of a hydrate, since nicotine and water mix with marked evolution of heat. In freshly prepared 20 per cent. solutions, the conversion does not seem to be completed at once but to require a certain time. From the increase in the rotation it must be concluded that the hydrate is more active than the pure base.[2]

G. Relations Between the Amount of Rotation and Chemical Constitution

77. Preliminary Remarks.—A large number of investigations have been carried out with these relations in view, but up to the present time without yielding very satisfactory results In establishing the rotating power of groups of bodies of given chemical constitution, certain regularities could be recognized, but almost always these were clouded by exceptions more or less numerous. The cause of this may rest in the uncertainty which is connected with the determination of the specific rotation of many substances. With solid bodies which can be investigated only in solutions, the rotation, as is well known, is in a large measure dependent on the concentration as on the nature of the inactive solvent, and such bod quently cannot be brought into comparison. Inves is largely limited, therefore, to active liquid bodies, a here there may be sometimes doubts as to their applic If, in their preparation, high heat is applied, or a reaction ensues, a partial racemization of the product sible, and in this case too low a result for the rotation obtained. (See § 28 and 29.)

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[1] Binz *Loc cit*

[2] Pribram Ber d. chem. Ges, 20, 1847

The reliability of the numerical value given for the rotation, if of a liquid substance, may be tested by exa several preparations made by different processes I direction, Purdie and Williamson[1] have carried out experiments with esters of malic and lactic acids, whic made·

1 By action of alkyl iodides on the silver salts of the

2 By esterification of a mixture of acid and alcohol of hydrochloric or sulphuric acid

By using also some observations of Walker,[2] a Anschutz and Reitter,[3] the following results were obtain

MALIC ACID ESTERS

	Silver salt method	Acid method		
	Purdie and Williamson $[\alpha]_D^{11^\circ}$	Purdie and Williamson $[\alpha]_D^{11^\circ}$	Walker $[\alpha]_D^{20^\circ}$	Ansc and R $[\alpha$
Methyl malate	— 7 34	·	— 6 85	—
Ethyl malate	— 12 42	— 10 34	— 10 18	— 1
N-Propyl malate...	— 13 70	..	— 11 62	— 1
N-Butyl malate....	— 12.20	..	..	— 1
Ethylacetyl malate	— 23 00	— 21 58	— 22 52	— 2
Ethylbutyryl "	— 22.70	..	— 22.22	·

---

[1] Purdie and Williamson J Chem Soc, **69**, 818 (1896)

[2] Walker: *Ibid*, **67**, 914 (1895)

[3] Anschütz and Reitter Ztschr phys Chem, **16**, 493 (1895)

LACTIC ACID ESTERS

	Silver salt method		Acid method.
	Walker	Purdie and Williamson.	Purdie and Williamson.
Ethyl lactate	— 14.52	- 13.46	10.33
Ethylacetyl lactate...........	..	— 49.87	49.75
Ethylchlor propionate........	+ 21 21 21.78	.	+ 19.41

The silver salt method, with the simple esters, gives, accordingly, somewhat higher values than the acid method. The lower rotation of the esters made by the latter method was not due to any racemization, since it was found that the acids separated from them showed no lower rotation than those originally employed. Besides, in the preparation of the above esters no high temperatures were applied (not above 100°); in other cases possibly greater differences will be noticed

As a further cause of the uncertainty in the specific rotation of liquid bodies, possible changes in the products, through polymerization, have been suggested. But as has been shown, however, in § 62, the effect of this reaction on the rotation has not been demonstrated with complete certainty. This has been confirmed lately by an observation made by Walden[1] on the diamyl ester of itaconic acid, as it was found that this substance, in spite of gradually increasing polymerization, still showed no indication of any, or at most of only an unimportant change in the optical activity In different conditions this compound gave the following rotations for a layer 1 dm. in length·

Freshly prepared, mobile liquid	α_D	4.80°
After 2 months, thick liquid, stringy		4.75
Completely hardened, colorless glass........		4.75

To test the relation between rotating power and chemical constitution, the esters of active amyl alcohol have been frequently employed. These have all been made from commercial left rotating amyl alcohol of different degrees of activity

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[1] Walden Ztschr phys Chem., 20, 383 (1896)

(for example, $[\alpha]_D = -4.5°$, Guye; $-4.78°$, Walden). Such preparations always contain a certain, but not determinable, proportion of inactive isomers, and are comparable among themselves to a limited extent only when secured from the same crude product. The different isomers of the crude amyl alcohol appear to be attacked by chemical reagents to not essentially different degrees, since Guye and Chavanne[1] found that the alcohols recovered by saponification of several esters, possessed a rotating power scarcely changed from that of the original.

In the following comparisons when bodies of different compositions are dealt with, the molecular rotation, $[M] = \frac{M}{100}[\alpha]$, is always employed, while for isomers, the value $[\alpha]$ is sufficient.

I Isomeric Bodies

An idea of the relations obtaining here, may be obtained from the following observations

78. *a. Metamerism. Structural Isomerism*

1 Translocation of the Active Radicals

Amylacetic acid	$[\alpha]_D = +8.53$	Walden Ztschr phys Chem, 15, 638
Amylacetate	$+2.50$	
Diamylacetic acid	$+18.27$	Walden Ztschr phys Chem, 15, 638.
Amylamyloacetate	$+7.01$	
Methyl valerate	$+16.83$	Guye and Chavanne Arch. phys nat, [4], 1, 54
Amyl formate	$+2.01$	

In these cases very marked differences appear.

2. Alcohol Radical Active Isomerism in the Inactive Acid Radical

Amyl normal butyrate	$[\alpha]_D = +2.97$	Walden Ztschr. phys. Chem., 15, 638.
Amyl isobutyrate	$+2.83$	
Amyl normal brombutyrate	$+2.27$	Walden Ztschr phys Chem, 15, 638
Amyl isobrombutyrate	$+2.53$	

The differences in rotation are small.

3. Alcohol Radical Inactive. Isomerism in the Active Acid Radical.

Methyl normal butyryl malate	$[\alpha]_D = -22.44$	Walden: Ztschr. phys. Chem, 17, 245.
Methylisobutyryl malate	-22.36	

---

[1] Guye and Chavanne: Bull Soc Chim, [3], 15, 275 (1896)

Ethyl normal butyryl malate..	— 22 22	Walden . Ztschr phys. Chem., 17, 245.
Ethylisobutyryl malate.......	— 21 99	
Ethyl-α-brom normal butyryl malate	— 24 76	Walden · Ztschr. phys. Chem., 17, 245.
Ethyl-α-bromisobutyryl malate	— 22.57	

The differences are likewise very small.

4 *Acid Radical Active Isomerism in the Inactive Alcohol Radical*

Normal butyl valerate.	$[\alpha]_D =$ + 10 60	Guye and Chavanne· Compt. rend , 116, 1454
Isobutyl valerate...........	+ 10 48	
Normal propyl glycerate.....	— 12 94	Frankland and Mac Gregor J. Chem Soc., 63, 524.
Isopropyl glycerate	— 11 82	
Normal butyl glycerate	— 11 02	Frankland and Mac Gregor· J. Chem Soc , 63, 524.
Isobutyl glycerate	— 14 23	
Secondary butyl glycerate...	— 10.58	
Normal propyl malate	— 11 62	Walden. Ztschr. phys Chem , 17, 245.
Isopropyl malate.....	— 10.41	
Normal propyl tartrate	+ 29.11	Freundler. Ann. chim phys , [7], 3, 433
Isopropyl tartrate...........	+ 34.83	
Normal butyl diacetyl tartrate	+ 8.0	Freundler. Ann chim phys , [7], 3, 433
Isobutyl diacetyl tartrate	+ 17 0	
Normal butyl dipropionyl tartrate	+ 6 9	Freundler: Ann. chim. phys., [7], 3, 433
Isobutyl dipropionyl tartrate	+ 11 4	
Normal butyldibutyryl tartrate	+ 6.0	Freundler. Ann chim. phys , [7], 3, 433
Isobutyl dibutyryl tartrate ..	+ 8 5	

The iso compounds show sometimes a higher, sometimes a lower, rotation than the normal.

b Position Isomerism in Benzene Derivatives

79. A number of investigations have been carried out to determine the influence of the *o*, *m* or *p* positions of an active and inactive group, or of two active groups in disubstituted benzene derivatives.

1 H Goldschmidt and Freund[1] have determined the specific rotation of the following solid bodies from chloroform solutions, the per cent strength, *p*, within each group being nearly the same.

In some groups the compounds, $C_6H_5.R$, were investigated to determine the effect of the addition of CH_3 by comparison with $C_6H_4{<}\begin{smallmatrix}R\\CH_3\end{smallmatrix}$.

---

[1] Ztschr phys Chem., 14, 394 (1894)

The differences show the increase or decrease in molecular rotation from one member to another.

		$[\alpha]_D$	$[M]_D$	δ
I.	*l*-Amylphenyl carbaminate	$+ 4.19$	$+ 8.7$	
$p=5.3$	*l*-Amyl-*o*-tolyl carbaminate	$+ 2.66$	$+ 5.9$	$- 2.8$
	“ *m*- “ $\left[C_6H_4{<}\begin{smallmatrix}CH_3\\NH\,COO.C_5H_{11}\end{smallmatrix}\right]$	$+ 3.85$	$+ 8.5$	$+ 2.6$
	“ *p*- “	$+ 4.47$	$+ 9.9$	$+ 1.4$
II.	*l*-Menthylphenyl carbaminate	$- 77.2$	$- 212.3$	
$p=5.6$	*l*-Menthyl-*o*-tolyl carbaminate	$- 65.9$	$- 190.4$	$- 21.9$
	“ *m*- “ $\left[C_6H_4{<}\begin{smallmatrix}CH_3\\NH\,COO\,C_{10}H_9\end{smallmatrix}\right]$	$- 71.4$	$- 206.4$	$+ 16.0$
	“ *p*- “	$- 72.3$	$- 208.9$	$+ 2.5$
III	Carbanilido-*d*-carvoxime	$+ 31.7$	$+ 89.9$	
$p=2.7$	Carbo-*o*-toluido-*d*-carvoxime	$+ 27.4$	$+ 81.7$	$- 8.2$
	“ *m*- $\left[C_6H_4{<}\begin{smallmatrix}CH_3\\NH\,CO\,NO\ C_{10}H_{14}\end{smallmatrix}\right]$	$+ 29.8$	$+ 88.8$	$+ 7.1$
	“ *p*-	$+ 30.8$	$+ 91.6$	$+ 2.8$
IV	Benzoyl-*d*-carvoxime	$+ 26.6$	$+ 71.7$	
$p=9$ to 10	*o*-Toluyl-*d*-carvoxime	$+ 27.1$	$+ 76.6$	$+ 4.9$
	m- “ $\left[C_6H_4{<}\begin{smallmatrix}CH_3\\CO\,NO\ C_{10}H_{14}\end{smallmatrix}\right]$	$+ 26.9$	$+ 76.0$	$- 0.6$
	p- “	$+ 23.4$	$+ 66.3$	$- 9.7$
V	*o*-Brombenzoyl-*d*-carvoxime	$- 26.0$	$+ 90.3$	
$p=5.5$	*m*- “ $\left[C_6H_4{<}\begin{smallmatrix}Br\\CO\,NO\ C_{10}H_{14}\end{smallmatrix}\right]$	$+ 18.2$	$+ 63.5$	$- 26.8$
	p- “	$+ 14.9$	$+ 51.9$	$- 11.6$
VI	*o*-Nitrobenzoyl-*d*-carvoxime	inactive		
$p=4.6$	*m*- “ $\left[C_6H_4{<}\begin{smallmatrix}NO_2\\CO\,NO\,.\,C_{10}H_{14}\end{smallmatrix}\right]$	$- 20.7$	$+ 64.9$	
	p- “	$+ 17.3$	$+ 54.4$	$- 10.5$

In general, the following relations appear from these observations.

a. With respect to the influence of position, the rotation increases in the order, *o*, *m*, *p*, in groups I, II, and III, but decreases in groups IV, V, and VI

b. The introduction of a methyl group is followed by a decrease in rotation in I, II, and III, and by an increase in IV.

2. The following esters of ditoluyl tartaric acid

$$\begin{array}{l}C_6H_4(CH_3)(CO)O{-}CH{-}COOH\\ \qquad\qquad\qquad\qquad\quad\ |\\ C_6H_4(CH_3)(CO)O{-}CH{-}COOH\end{array}$$

have been investigated in fused condition at different temperatures by Frankland and Malcolm[1]

Methyl ester	Temp	100°		137°		183°	
o Compound...	$[\alpha]_D =$	− 68.0		− 61 7		− 52.8	
m Compound..	$[\alpha]_D =$	− 79 0	11.0	− 70 6	8 9	− 61 0	8.2
p Compound ..	$[\alpha]_D =$	− 102 8	23.8	− 91 5	20 9	− 76 9	15.9
Ethyl ester							
o Compound ..	$[\alpha]_D =$	− 54 7		− 50 4		..	
m Compound..	$[\alpha]_D =$	− 63 7	9.0	− 58 7	8 3	..	
p Compound ..	$[\alpha]_D =$	− 90 0	26.3	− 81 5	22 8	− 69 5	

Here the rotation increases in the order *o*, *m*, *p*, and the difference between *o* and *m* is always smaller than the difference between *m* and *p*. These relations remain true for the different temperatures

3 The specific rotations of the following bodies have been determined by Binz[2] from chloroform solutions

		$[\alpha]_D$	
o Oxybenzylidenefenchylamine	($p = 2.5$)...... ..	+ 66.0	
p $\left[C_6H_4 \begin{matrix} OH \\ CH\ N.C_{10}H_{17} \end{matrix}\right]$	($p = 1\ 3$)....... ...	+ 72 0	6 0
o Methoxybenzylidenefenchylamine	($p = 5$)	+ 59 4	
p $\left[C_6H_4 \begin{matrix} O\ CH_3 \\ CH\ N\ C_{10}H_{17} \end{matrix}\right]$	($p = 5$)	+ 78.1	18 7

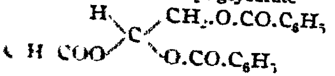
4 Walden[3] obtained from solutions in glacial acetic acid 1 . for

Malic acid di-*o*-toluide	$[\alpha]_D = -\ 66.5$	
Malic acid di-*p*-toluide	$-\ 70\ 0$	3 5

In the majority of these isomers the para compound appears to have a greater rotation than the ortho.

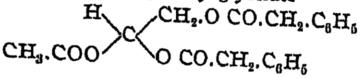
But cases are known in which isomeric bodies rotate in opposite directions This is found[4] in

Propyldibenzoyl glycerate



$[\alpha]_D = -\ 21.0$

Methyldiphenylacetyl glycerate



$[\alpha]_D = -\ 16.1.$

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[1] J Chem Soc, 69, 1309 (1896)

[2] Binz Ztschr phys. Chem, 12, 727 (1893)

[3] Walden Ztschr phys Chem., 17, 245 (1895)

[4] Frankland and MacGregor J. Chem Soc, 69, 104 (1896)

Also with the isomers in the santonin group, for which there was obtained from chloroform solutions:

Santonin[1]	$[\alpha]_D = -171.4°$
Metasantonin	$+118.8$
Santonide	$+744.6$
Metasantonide	-223.5
Parasantonide	$+897.3$

c. Stereoisomeric Bodies

80. A series of observations carried out by Walden,[2] are concerned with the active amyl esters of fumaric and maleic acids and their derivatives. *l*-amyl alcohol was employed in their preparation.

Diamyl ester of	$[\alpha]_D$	$[M]_D$	Diff $F-M$
Fumaric acid[3]	+ 5.93	+ 15.17	+ 3.35
Maleic acid	+ 4.62	+ 11.82	
Chlorfumaric acid[3]	+ 5 78	+ 16.78	+ 5.08
Chlormaleic acid	+ 4.03	+ 11.70	
Bromfumaric acid	+ 5.99	+ 20.07	+ 4.71
Brommaleic acid	+ 4.58	+ 15.36	
Methylfumaric (mesaconic acid)	+ 5.93	+ 16.01	+ 4.84
Methylmaleic acid (citraconic acid)	+ 4.14	+ 11.17	
			Mean 4 50

In all these bodies, it is seen that the fumaroid form has a molecular rotation higher by about 4.5 than the maleinoid.

On the other hand, if we consider compounds which are related to these types, but which are saturated (acids of the succinic series), according to Walden, the above no longer holds true, as seen in the following:

Diamyl ester of	$[\alpha]_D$	$[M]_D$	Diff $F-M$
p-Dimethylsuccinic acid	+ 3.66	+ 10.47	+ 0.68
Antisuccinic acid	+ 3 42	+ 9.79	
Racemic acid	+ 3 37	+ 9.77	— 4.06
Mesotartaric acid	+ 4.77	+ 13 83	

---

[1] Carnelutti and Nasini Ber d chem Ges, **13**, 2208 (1880)

[2] Walden · Ztschr phys. Chem, **20**, 377 (1896)

[3] Earlier observations of Walden (Ztschr phys Chem, **15**, 638 (1894)) gave the following values for these bodies

Diamyl esters of	$[\alpha]_D$	$[M]_D$	Diff
Fumaric acid	+ 5.69	+ 14 56	3.43
Maleic acid	+ 4 35	+ 11 13	
Chlorfumaric acid	+ 5.74	+ 16 67	3.31
Chlormaleic acid	+ 4 60	+ 13 36	

But it must be remembered here, however, according to § 18, that a racemic acid ester of active amyl alcohol does not exist. This is a mixture of the amyl esters of *d*- and *l*-tartaric acid, which bodies, since they are not reflection images of each other, cannot form a racemic compound.

II. Homologous Series

81. The relations appearing here can be seen from the following observations:

CHANGES IN THE MOLECULAR ROTATION WITH INCREASE OF CH_2

	$[\alpha]_D$	$[M]_D$	Diff
1.[1]Amyl formate	+ 2.01	+ 2.33	
Amyl acetate	2.53	3 29	+ 0.9
Amyl propionate	2.77	3 99	+ 0.7
Amyl *N*-butyrate	2.69	4.25	+ 0.2
Amyl *N*-valerate	2.52	4 33	+ 0 0
Amyl *N*-caproate	2.40	4.46	+ 0.1
Amyl *N*-heptylate	2.21	4.42	− 0.0
Amyl *N*-caprylate	2.10	4 49	+ 0.0
Amyl *N*-nonylate	1.95	4.44	− 0 0
Amyl laurate	1.56	4.21	
Amyl palmitate	1.28	4 17	
Amyl stearate	1 27	4.49	
2.[2]Valeric acid	+ 13.64	+ 13.91	
Methyl valerate	16 83	19.53	+ 5.6
Ethyl valerate	13.44	17.47	− 2.
N-Propyl valerate	11.68	16.82	− 0 6
N-Butyl valerate	10.60	16 75	− 0.
3 [3]Methyl glycerate	− 4.80	− 5.76	
Ethyl glycerate	9.18	12 30	+ 6.
N-Propyl glycerate	12 94	19.15	+ 6 8
N-Butyl glycerate	13.19	21.37	+ 2.
Heptyl glycerate	11.30	23 05	
Octyl glycerate	10 22	22.28	− 0.
4 [4]Methyl diacetylglycerate	− 12 04	− 24.56	
Ethyl diacetylglycerate	16.31	35 56	+ 11.
N-Propyl diacetylglycerate	19.47	45.17	+ 9.
5 [5]Methyl dibenzoylglycerate	+ 26 89	+ 88.20	
Ethyl dibenzoylglycerate	26.58	90.90	+ 2
N-Propyl dibenzoylglycerate	21.00	74 76	− 16.

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[1] Guye and Chavanne: Compt. rend, **120**, 452, Bull Soc Chim., (3), **15**, 275 (189

[2] Guye and Chavanne. Compt. rend, **116**, 1454 (1893)

[3] Frankland and MacGregor: J. Chem. Soc, **63**, 1415 (1893)

[4] Frankland and MacGregor· J. Chem. Soc, **63**, 1430

[5] Frankland and MacGregor: J. Chem. Soc., **69**, 104 (1896).

	I $[\alpha]_D$	II $[\alpha]_D$	III $[\alpha]_D$
6. Methyl malate ..	— 6 85	— 6.88	— 7.34
Ethyl malate....	10.18	10.65	12.42
N-Propyl malate	11.62	11.60	13.70
N-Butyl malate	..	10 72	12.20
Amyl malate ...	9.92	..	..
Capryl malate ..	6.92	..	..

	$[M]_D$		$[M]_D$		$[M]_D$	
Methyl malate ..	— 11 10	+ 8 25	— 11.15	+ 9.08	— 11.89	+ 11.67
Ethyl malate....	19 35	+ 5 97	20.23	+ 5.06	23.56	+ 6.31
N-Propyl malate	25.32		125.29	+ 1.09	29 87	+ 0.14
N-Butyl malate	..		26.38		30 01	
Amyl malate ...	27.19	— 2.42	..		..	
Capryl malate ..	24 77		..		..	

I. Formed by esterification from acid and alcohols by aid of sulphuric acid.[1]

II. Produced in same way.[2]

III. By action of the alkyl iodides on silver malate.[3]

	$[\alpha]_D$		$[M]_D$			
7. Diacetyl malate of	I.[4]	II [5]	I [4]		II.[5]	
Methyl......	— 22 92	— 22.86	— 46 76	+ 5 49	— 46.64	— 5 79
Ethyl....	22 52	22 60	52 25	+ 7 15	52 43	+ 6 53
N-Propyl ...	22 85	22 68	59.40	+ 3.61	58 96	— 1 58
N-Butyl....	21.88	19 93	63.01		57.38	

	$[\alpha]_D$	$[M]_D$	
8 [6]Methyl *d*-tartrate.........	+ 2.14	+3 8	+ 11.9
Ethyl *d*-tartrate......................	7.66	15 7	+ 13 3
N-Propyl *d*-tartrate	12 44	29 0	
9.[7]Methyl chlorsuccinate.................	+ 41.42	+74.8	— 17 5
Ethyl chlorsuccinate........	27.50	57.3	+ 3.3
N-Propyl chlorsuccinate..............	25 63	60.6	— 3.5
N-Butyl chlorsuccinate..............	21.57	57.1	
Amyl chlorsuccinate	21.56	63.1	2 act rad.

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[1] Walden Ztschr phys. Chem , 17, 245 (1895)

[2] Anschütz and Reitter Ztschr phys Chem , 16, 493 (1895)

[3] Purdie and Williamson, J Chem Soc., 69, 818 (1896)

[4] Walden , Ztschr phys Chem , 17, 245 (1895)

[5] Anschutz and Reitter Ztschr phys Chem , 16, 493 (1895)

[6] M A Pictet Arch phys nat , (3), 7, 82 (1882)

[7] Walden Ztschr phys Chem , 17, 245

	$[\alpha]_D$	$[M]_D$	
10.[1] Santonic acid	− 70.31	− 185.6	
Methyl santonate	52.33	145.5	− 40 1
Ethyl santonate	45.35	132.4	− 13.1
N-Propyl santonate	39.34	120.4	− 12 0
Parasantonic acid	89 51	260.1	
Methyl parasantonate	108.91	302.8	+ 42.7
Ethyl parasantonate	99 98	291.9	− 10.9
N-Propyl parasantonate	91.27	279.3	− 12.6

From chloroform solutions.

	$[\alpha]_D$	$[M]_D$	
11. Fenchylamine (liquid)[2]	− 24.89	− 38 0	
Formylfenchylamine ($p = 3.9$)	36 56	66.0	
Acetyl " ($p = 4.6$)	46.62	90.7	+ 24.7
Propionyl " ($p = 5.0$)	53.16	110 9	+ 20.2
Butyryl " ($p = 1.8$)	53 11	118.2	+ 7.3

Determined from chloroform solutions.

The following relations appear by comparing the molecular rotations of the above compounds :

With the homologous esters, the values of $[M]$ sometimes increase and sometimes decrease with increasing molecular weight of the alcohol radical.

An *increase* is found in the esters of glyceric acid (No 3), diacetyl glyceric acid (No. 4), malic acid (No. 6), diacetyl malic acid (No. 7), and tartaric acid (No. 8) ; also with the amyl esters of the fatty acids (No. 1), and the fenchyl derivatives (No. 11).

A *decrease* is found with the esters of valeric acid (No. 2), santonic and parasantonic acids (No. 10).

The differences between the molecular rotations of two neighboring members of a series, decrease in most cases regularly (Nos. 1, 2, 4, 6, 11) ; the effect of the gradually increasing molecular weight of the alcohol radical becomes therefore, constantly less.

From a certain molecular weight on, the influence seems to be exerted in the opposite direction, so that the increase is changed to a decrease, from which it follows that in the homologous series a member is found which possesses a maximum rotation.

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[1] Carnelutti and Nasini · Ber d chem Ges, 13, 2208 (1880)

[2] Binz · Ztschr. phys. Chem., 12, 731 (1893).

The geatest change is found in going from the acid to the first ester (Nos. 2 and 10).

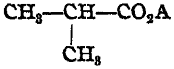
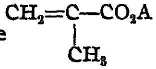
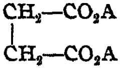
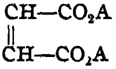
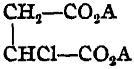
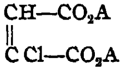
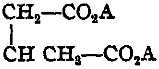
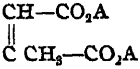
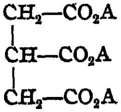
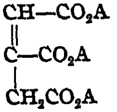
In Nos. 5 and 9 the rate of change is irregular.

III. The Effect of Linkage of the Carbon Atoms.

The experimental results on this are as follows :-

a. Change from Single to Double Bond by Loss of 2 Atoms of H.

82. The changes of rotation in cases of this kind have been investigated by Walden[1] in a series of liquid esters of active amyl, $CH(CH_3)(C_2H_5)—CH_2—$, in the preparation of which left-rotating amyl alcohol was used.

	$C_5H_{11} = A$	$[\alpha]_D$	$[M]_D$	Diff.
Amyl *n*-butyrate	$CH_3—CH_2—CH_2—CO_2A$	+ 2.81	+ 4.43	2.19
Amyl crotonate	$CH_3—CH{=}CH—CO_2A$	+ 4.24	+ 6.62	
Amyl isobutyrate	 $\begin{array}{l} CH_3—CH—CO_2A \\ \qquad \vert \\ \qquad CH_3 \end{array}$	+ 3.10	+ 4.90	0.57
Amyl methacrylate	 $\begin{array}{l} CH_2{=}C—CO_2A \\ \qquad \vert \\ \qquad CH_3 \end{array}$	+ 3.51	+ 5.47	
Diamyl succinate	 $\begin{array}{l} CH_2—CO_2A \\ \vert \\ CH_2—CO_2A \end{array}$	+ 3.76	+ 9.71	5.46
Diamyl fumarate	 $\begin{array}{l} CH—CO_2A \\ \Vert \\ CH—CO_2A \end{array}$	+ 5.93	+ 15.17	
Diamyl chlorsuccinate	 $\begin{array}{l} CH_2—CO_2A \\ \vert \\ CHCl—CO_2A \end{array}$	+ 3.75	+ 10.98	5.80
Diamyl chlorfumarate	 $\begin{array}{l} CH—CO_2A \\ \Vert \\ C\,Cl—CO_2A \end{array}$	+ 5.78	+ 16.78	
Diamyl methylsuccinate	 $\begin{array}{l} CH_2—CO_2A \\ \vert \\ CH\ CH_3—CO_2A \end{array}$	+ 3.76	+ 9.99	6.02
Diamyl mesaconate	 $\begin{array}{l} CH—CO_2A \\ \Vert \\ C\ CH_3—CO_2A \end{array}$	+ 5.93	+ 16.01	
Triamyl tricarballylate	 $\begin{array}{l} CH_2—CO_2A \\ \vert \\ CH—CO_2A \\ \vert \\ CH_2—CO_2A \end{array}$	+ 4.01	+ 15.48	8.18
Triamyl aconitate	 $\begin{array}{l} CH—CO_2A \\ \Vert \\ C—CO_2A \\ \vert \\ CH_2CO_2A \end{array}$	+ 6.16	+ 23.66	

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[1] Walden Ztschr. phys Chem, 20, 569 (1896).

	$C_5H_{11} = A$	$[\alpha]_D$	$[M]_D$	Diff.
Amyl hydrocinnamate	$C_6H_5—CH_2—CH_2—CO_2A$	$+ 2.26$	$+ 4.98$	11.38
Amyl cinnamate	$C_6H_5—CH{=}CH—CO_2A$	$+ 7.51$	$+ 16.36$	

In all these cases it is seen that the change from single linkage of carbon atoms to double linkage is followed by an increase in the rotating power.

b Change from Double to Triple Bond between Carbon Atoms.

83. For this case, we have as yet only the following illustration, likewise from Walden:[1]

		$[\alpha]_D$	$[M]_D$	Diff.
Amyl cinnamate	$C_6H_5—CH{=}CH—CO_2A$	$+ 7\ 51$	$+ 16.36$	4.31
Amyl phenylpropiolate	$C_6H_5—C{\equiv}C—CO_2A$	$+ 5.58$	$+ 12.05$	

Here a decrease in activity follows

c. Change from a Chain Carbon Compound to a Cyclic Compound.

84. As van't Hoff[2] first showed, the ring structure exerts a very considerable influence on the degree of rotation, and it may even change its sign

Accurate numerical data are here hard to obtain, as most of the compounds which could be considered are solid, and their specific rotations, therefore, variable with the solvent and concentration. The relations which may obtain may be seen from the following comparison of two dicarboxylic acids with their cyclic anhydrides:

Diacetyl tartaric acid	water	$c = 17.95$	$[\alpha]_D = - 23.0$
	water	$c = 3.76$	$- 19.3$
	ethyl alcohol	$c = 7.37$	$- 23.6$
	ethyl alcohol	$c = 3.27$	$- 21.5$
Diacetyl tartaric anhydride	acetone	$c = 11.66$	$[\alpha]_D = + 59.7$
	acetone	$c = 4.40$	$+ 62.0$
	benzene	$c = 2.09$	$+ 58.7$
	benzene	$c = 1.05$	$+ 63.1$
Dibenzoyl tartaric acid (anhydrous)	ethyl alcohol	$c = 4.76$	$[\alpha]_D = - 117.7$
	methyl alcohol	$c = 4.63$	$- 122.1$
Dibenzoyl tartaric anhydride[3]	acetone	$c = 4.64$	$[\alpha]_D = + 142\ 9$

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[1] Walden *Loc cit*

[2] van't Hoff "Lagerung der Atome im Raume," 1894, p. 109.

[3] M A Pictet Jahresbericht, 1882, p 856.

In both of these cases the rotation of the anhydride is greater than that of the acid, and of opposite direction.

But another condition appears with the following bodies :[1]

Chlorsuccinic acid[2]	acetic ether	$c = 10$	$[\alpha]_D = + 52.7$
	acetic ether	$c = 6.66$	$+ 52.9$
Chlorsuccinic anhydride	acetic ether	$c = 10$	$[\alpha]_D = + 30.9$
	acetic ether	$c = 5$	$+ 33.6$

In this case the rotation of the anhydride is smaller than that of the acid, but in the same direction.

If we compare the lactone-forming acids of the sugar group with the lactones themselves, it is found, as pointed out in § 75, that the latter have always much the stronger activity. As the true rotating power of the acid can not be determined with certainty because of the existence of multirotation, Alberda van Ekenstein, Jorissen and Reicher[3] have investigated the neutral alkali salts, which do not show multirotation, and from which the rotation of the acid ion may be obtained. The lactones were tested as soon as possible after solution so as to avoid the effects of multirotation. In the experiments the concentration of the acid ions was from 2 to 6.5 grams in 100 cc. and of the lactones from 4 to 10 grams. With addition of a few data from Fischer, Tollens, and others, the authors mentioned give the following table [4]

	$[M]_D$		Change in rotation
	Acid ion	Lactone	
Ribonic acid	+ 2°	− 30°	32°
d-Gluconic acid	+ 16	+ 116	100
l-Mannonic acid	+ 20	− 97	117
d-Gulonic acid	− 27	+ 99	126
l-Gulonic acid	+ 27	− 99	126
Saccharonic acid	− 11	+ 152	163
Isosaccharonic acid	− 11	+ 102	113
d-Saccharic acid	+ 26	+ 77	51
Mannosaccharic acid	+ 2	+ 354[5]	352
α-Rhamnohexonic acid	+ 13	+ 163	150
α-Glucoheptonic acid	+ 16	− 112	128

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[1] Walden, Ztschr phys Chem, 17, 245 (1895)

[2] Chlorsuccinic acid dissolved in water has a much smaller rotation than in acetic ether. Walden (Ber. d chem Ges, 26, 215) gives these values.

Water	$c = 16$	$[\alpha] = + 20.6$
	$c = 6.4$	$+ 20.8$
	$c = 3.2$	$+ 21.3$

[3] Ztschr phys Chem, 21, 383 (1896)

[4] The table contains the mean values of the numbers given in the original paper.

[5] This refers to the double lactone, $C_6H_6O_6$

The rotating power of the cyclic lactones is thus seen to be much stronger than that of the acid ion and often in the opposite direction. The change of rotation is mostly from 100° to 150°, but the numbers disclose no characteristic regularities.

In carbocyclic and heterocyclic compounds high rotating power is generally found, especially when these compounds contain several asymmetric carbon atoms, as is the case in the bodies of the santonin group and in the alkaloids, for example :[1]

	$[\alpha]_D$
Limonene-α-nitrosochloride in chloroform	± 314°
Limonene-β-nitrosochloride in chloroform	± 241
Sodium nitrocamphor in water	+ 233
Metasantonide in chloroform	− 224
Santonide in chloroform	+ 745
Parasantonide in chloroform	+ 897
Quinidine in alcohol	+ 255
Thebaïne in alcohol	− 219
Cupreïne sulphate in water	− 290

But, on the other hand, some cyclic bodies possess a low rotating power, as ·

	$[\alpha]_D$
Tetrahydronaphthylenediamine hydrochloride in water	− 7.5°
Benzoylhydrochlorcarvoxime in acetic ether	+ 9.9
Aconitine in alcohol	+ 11.0
Cinchonicine in water	+ 28.7
Cocaïne in chloroform	− 16.3
Conine, liquid	+ 18.3

High rotation is found also in bodies which are not cyclic, as :

Cystin in hydrochloric acid	− 205.9
α-Phenylchloracetylchloride in carbon disulphide	+ 158.3

d. Compounds with Several Asymmetric Carbon Atoms.

85. **Summation of the Rotating Power of Active Groups. Optical Superposition.**—In his original statement of the doctrine of asymmetric carbon atoms, van 't Hoff[2] made the assumption that in compounds which contain several asymmetric groups, the optical effect of each one is not changed by the presence of the others, and the rotation of the whole is equal to the alge-

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[1] For the references to the literature see the chapter on constants of rotation

[2] van 't Hoff : Bull. Soc. Chim, [2], 23, 298 (1875), "Lagerung der Atome im Raume" 2nd ed. p 120.

braic sum of the group rotations, as these may have opposite signs.

The correctness of this assumption, which lies at the foundation of all discussions on optical isomerism, has received experimental proof recently through work of Guye and of Walden. These chemists made isomeric liquid amyl esters, partly from active, partly from inactive components, in the following three combinations:

I. From active acid and inactive alcohol.
II From inactive acid and active alcohol.
III. From active acid and active alcohol.

Ester III contains the asymmetric groups of I and II united, and the sum of the specific rotations of I and II must equal the specific rotation of III.

As the following experiments show this condition actually obtains. In the preparation of esters of inactive acids or of inactive amyl alcohol, the racemic forms of these compounds were used. (On the racemization of amyl alcohol see § 28.)

AMYL LACTATES[1]

		$[\alpha]_D$
I.	*i*-Amyl *l*-lactate	− 6.38°
II	*l*-Amyl *i*-lactate	+ 2.64
III.	*l*-Amyl *l*-lactate	− 3.93
	I + II =	− 3.74

AMYL VALERATES[2]

I	*i*-Amyl *d*-valerate α_D for $l = 0.5$ dm =	+ 4.40°
II.	*l*-Amyl *i*-valerate	+ 1.22
III.	*l*-Amyl *d*-valerate	+ 5.32
	I + II =	+ 5.62

AMYL α-OXYBUTYRATES[3]

		$[\alpha]_D$
I.	*i*-Amyl *l*-oxybutyrate	− 8.5°
II.	*l*-Amyl *i*-oxybutyrate	+ 1.5
III.	*l*-Amyl *l*-oxybutyrate	− 7.3
	I + II =	− 7.0

AMYL AMYLACETATES.[4]

		$[\alpha]_D$
I	*i*-Amyl *d*-amylacetate	+ 4.36°
II.	*l*-Amyl *i*-amylacetate	+ 1.54
III.	*l*-Amyl *d*-amylacetate	+ 5.64
	I + II =	+ 5.90

[1] Walden: Ztschr phys Chem., **17**, 721 (1895)
[2] Guye and Gautier Compt rend, **119**, 953 (1894).
[3] Guye and Jordan Compt rend, **120**, 632 (1895)
[4] Guye: Compt. rend, **121**, 827 (1895)

Amyl Phenylchloracetates[1]

	$[\alpha]^D$
I. *i*-Amyl *d*-phenylchloracetate	+ 23.31°
II. *l*-Amyl *i*-phenylchloracetate	+ 3.23
III. *l*-Amyl *d*-phenylchloracetate	+ 26.79
I + II =	+ 26.54

Amyl Mandelates.[2]

	$[\alpha]_D$
I. *i*-Amyl *l*-mandelate	− 96.46°
II. *l*-Amyl *i*-mandelate	+ 2.76
III. *l*-Amyl *l*-mandelate	− 94.02
I + II =	− 93.70

Diamyl Chlorsuccinates.[3]

	$[\alpha]_D$
I. *i*-Amyl *d*-chlorsuccinate	+ 21.56°
II *l*-Amyl *i*-chlorsuccinate	+ 3.75
III. *l*-Amyl *d*-chlorsuccinate	− 25.15
I + II =	+ 25.31

Diamyl Amylmalonates[4]

	$[\alpha]_D$
I. *i*-Amyl *d*-amylmalonate	+ 6.10°
II. *l*-Amyl *i*-amylmalonate	+ 3.48
III. *l*-Amyl *d*-amylmalonate	+ 9.65
I + II =	+ 9.58

Diamyl Malates.[5]

	$[\alpha]_D$
I. *i*-Amyl *l*-malate	− 9.92°
II. *l*-Amyl *i*-malate	+ 3.50
III. *l*-Amyl *l*-malate	− 6.88
I + II =	− 6.42

Diamyl Tartrates

	$[\alpha]_D$[6]	$[\alpha]_D$[7]
I. *i*-Amyl *d*-tartrate	+ 14.10°	+ 14.67°
II. *l*-Amyl *i*-tartrate	+ 3.37	+ 3.38
III *l*-Amyl *d*-tartrate	+ 17.73	+ 18.61
I + II =	+ 17.47	+ 18.05

Diamyl Divaleryl Tartrates.[8]

(Six Asymmetric Carbon Atoms.)

	$[\alpha]_D$
I. *l*-Amyl *i*-valeryl *i*-tartrate	+ 2.44°
II *i*-Amyl *d*-valeryl *i*-tartrate	+ 3.48
III. *i*-Amyl *i*-valeryl *d*-tartrate	+ 6.42
IV. *l*-Amyl *d*-valeryl *d*-tartrate	+ 11.32
I + II + III =	+ 12.34

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[1] Walden Ztschr. phys Chem, **17**, 722 (1895)

[2] Walden · Ztschr. phys Chem, **17**, 721 (1895).

[3] Walden · Ztschr. phys Chem, **17**, 723 (1895)

[4] Guye Compt. rend, **121**, 827 (1895).

[5] Walden : Ztschr. phys Chem, **17**, 722 (1895)

[6] Walden : Ztschr. phys Chem, **17**, 723 (1895).

[7] Guye. Compt. rend, **122**, 932 (1896)

[8] Guye and Goudet Compt rend., **122**, 932 (1896).

Finally, optical superposition may be recognized in the following bodies also, if, on account of differences in composition, the molecular rotation $[M]$, be made the basis of comparison:

	$[M]_D$[1]
I. Amyl acetate	+ 3.25°
II. Amyl acetic acid	+ 11.08
III. Amyl amylacetate	+ 14 02
	I + II = + 14 33

The great differences which appear in the specific rotations of the isomeric sugars, for example in the hexoses, or in the hexonic acids, depend, undoubtedly, as van't Hoff[2] suggested, on the summation of the effects of the four asymmetric groups contained in them, the rotations of which are unequally strong and in opposite directions. Observations are not yet sufficiently numerous to establish the values of the group rotations, not even for the ions of the lactone-forming acids given some pages back.

IV Dependence of the Rotatory Power of an Active Atomic Complex on the Masses of the Four Radicals Joined to the Asymmetric Carbon Atom.— The Hypothesis of Guye.

86.—An attempt to determine the amount and direction of rotation from the composition of an active molecule was made in 1890, simultaneously by Ph A. Guye[3] and Crum Brown,[4] a consideration of the tetrahedral form of the asymmetric complex, and the relative masses of the four groups being the common starting point in the discussion. The problem, which was handled in detail and brought into mathematical form especially by Guye,[5] was well calculated to arouse great interest, and it has been the incentive in the undertaking of numerous investigations.

The hypothesis, as stated by Guye[6] in 1893, in general form is as follows:

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[1] Walden Ztschr. phys Chem , **15**, 638 (1894)

[2] van't Hoff "Lagerung der Atome im Raume," 2d ed p 120

[3] Guye First paper Compt rend , **110**, 714 (1890).

[4] Crum Brown Proc Roy Soc Edin , **17**, 181 (1890)

[5] Guye Compt. rend, **111**, 745 (1891) , **114**, 473 (1892) , **116**, 1133, 1378, 1451, 1454 (1893); **119**, 906 (1894) , **120**, 157, 452, 632, 1274 (1895) Thèse Paris, 1891 Conférences de la Soc Chim , Paris, 1891, p. 149 Arch. sc. phys nat. [3] **26**, 97, 201, 333 (1891). Ann. chim. phys., [6], **25**, 145 (1892) Bull Soc Chim , [3], **9**, 403 (1893)

[6] Guye . Compt. rend , **116**, 1378, 1451.

As a measure of the amount and sign of the rotating power of an active molecule, the so-called *product of asymmetry*, P, may be taken, which, in general, may be defined as equal to the product of the six perpendiculars from the center of gravity of a tetrahedron to the six planes of symmetry of the original regular tetrahedron. According to the orientation of the four groups combined with the asymmetric carbon atom, P is found in different ways:

1. If the tetrahedron is regular and the radicals are found exactly at the angles of the same, the product of asymmetry depends only on the masses of the four groups, a, b, c, and d; that is, on their formula weights. In this case, the following expression[1] is found for P.

$$(I) \quad P = \frac{(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{(a+b+c+d)^6}(l. \sin \alpha)^6$$

in which the constant factor $(l. \sin \alpha)^6$ may be dropped.[2]

2. The masses, a, b, c, and d may be situated at different distances, l, m, n, and p, from the center of gravity of the original tetrahedron, but always in the direction of the straight lines from the center to the four angles.

3. The masses a, b, c and d are found at different distances, l, m, n and p from the center of the original tetrahedron, and further, on account of their mutual attractions, they have undergone lateral displacements, so that the straight lines, l, m, n and p form different angles with each of the original planes of symmetry ($\alpha_1 \ldots \alpha_6$ for l; $\beta_1 \ldots \beta_6$ for m; $\gamma_1 \ldots \gamma_6$ for n; $\delta_1 \ldots \delta_6$ for p).

The complicated formulas[3] for P in case 2 and the perfectly general case 3 can not be used for calculations because they contain undeterminable quantities (l, m, n, p $\alpha \ldots \beta \ldots \gamma \ldots \delta$). We are, therefore, limited to formula I, under the assumption that the displacing influences mentioned in cases 2 and 3 are too small to cause appreciable disturbances.

The above equation satisfies the conditions, that:

a. The product P must be zero when two or more of the masses, *a*, *b*, *c*, and *d* are equal; that is, when the asymmetry of the molecule is destroyed.

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[1] For the derivation of the formula, the original paper must be consulted.

[2] In this, l is the distance of the four masses from the center of the tetrahedron, and α is the angle 54° 44′.

[3] See the original paper

b. The product must be the same but of opposite sign when two of the values *a*, *b*, *c*, and *d* are transposed, the one for the other. Such a change corresponds to the conversion of the right-rotating form of a body into the isomeric left-rotating.

Changes in the rotating power must follow parallel with changes in the product, *P*, corresponding to variations in the weights *a*, *b*, *c*, and *d*. If the order of the weights of the groups is as follows:

$$a > b > c > d$$

and *a* is replaced gradually by smaller and smaller values, then, if the original body be assumed, for illustration, as right-rotating, the following conditions are to be expected:

1. As long as $a > b$ there must be, according to the numerical relation between them, either a continuous decrease in the right rotation, or at first an increase, and then after passing a maximum, a decrease in the rotation.

2 $a = b$. Condition of inactivity

3. $a < b$. Change to increasing left rotation to a maximum, then a decrease

4 $a = c$. Second condition of inactivity.

5. $a < c$ Appearance of right rotation, which increases to a maximum and then decreases.

6 $a = d$. Third condition of inactivity.

7. $a < d$. Increasing left rotation

In the experimental examination of these provisions, they seemed at first to be confirmed. Thus, it was possible to show in some homologous series the complete or nearly complete coincidence of a maximum point in rotation with a maximum point in the product of asymmetry, as is illustrated by the following table of Guye and Chavanne[1] based on observations by Frankland and MacGregor[2] on the rotation of esters of *l*-glyceric acid. The value of the product of asymmetry, *P*, is shown in parallel column, and multiplied by 10^6 to give convenient numbers for comparison.

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[1] Guye and Chavanne Compt. rend, **116**, 1454

[2] Frankland and MacGregor J Chem Soc **63**, 524 (1893).

Glycerate of	*a* C(COOR).	*b* $(CH_2OH.)$	*c* (OH)	*d* (H.)	$[\alpha]_D$.	$[M]_D$.	$P. 10^6$
N-Butyl...	101	31	17	1	— 11.02[1]	— 17.9	347
N-Propyl..	87	31	17	1	— 12.94	— 19.2	358
Ethyl	73	31	17	1	— 9.18	— 12.3	345
Methyl....	59	31	17	1	— 4.80	— 5.8	289

A very near coincidence in the maximum points, with a displacement of only one term, is shown in the following valeric esters investigated by Guye and Chavanne.[2]

Valerate of	*a* C(COOR)	*b* (C_2H_5)	*c* (CH_3)	*d* (H.)	$[\alpha]_D$.	$[M]_D$	$P. 10^6$.
N-Butyl...	101	29	15	1	+ 10.60	+ 16.75	351
N-Propyl..	87	29	15	1	11.68	16.82	364
Ethyl	73	29	15	1	13.44	17.47	374
Methyl....	59	29	15	1	16.83	19.53	332
Valeric acid	45	29	15	1	13.64	13.91	218

Also when the specific rotations of the amyl esters of the fatty acids are compared with their products of asymmetry we find.[3]

	$[\alpha]_D$	$P. 10^6$
Amyl *n*-laurate..	+ 1.56	144
Amyl *n*-nonate..	1.95	204
Amyl *n*-caprylate	2.10	229
Amyl *n*-heptate	2.21	258
Amyl *n*-caproate	2.40	289
Amyl *n*-valerate...	2.52	321
Amyl *n*-butyrate	2.69	351
Amyl propionate	2.77	373
Amyl acetate	2.53	374
Amyl formate..	2.01	332

Numerous other investigations of these relationships in which besides Guye,[1] many chemists,[2] and especially Walden[3] have taken part led gradually to the discovery of numerous facts which can not at all be reconciled with the requirements of the hypothesis. The following discrepancies, especially, were brought out:

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[1] Frankland and MacGregor gave later the corrected values for *N*-butyl glycerate $\alpha = -13.19°$ and $[M]_D = -21.4°$ (J. Chem. Soc., 63, 1417), which makes this example unsuitable for confirmation of the hypothesis.

[2] Guye and Chavanne Compt rend., 116, 1454.

[3] Guye and Chavanne Compt rend., 119, 906. If the values of the molecular rotation $[M]$ be taken, the maximum is then found at amyl caprylate, that is, far removed from the maximum of the product of asymmetry.

1. Compounds in which two of the groups a, b, c, and d, have the same weight, and which, accordingly, should be inactive, often possess a strong rotating power.—Walden[4] gives many cases, for example.

	$[\alpha]_D$	$[M]_D$
Dimethyl acetylmalate $a \quad b \quad c \quad d$ $C(CH_2.COOCH_3)\ (CO.OCH_3)\ (O\ C_2H_3O)\ (H)$ 73 59 59 1	— 22.9	— 46.8
Methyl acetylmandelate $C(C_6H_5)\ (CO.OCH_3)\ (O.C_2H_3O)\ (H)$ 77 59 59 1	— 146.4	— 304.5
Ethyl propionylmandelate $C(C_6H_5)\ (CO.OC_2H_5)\ (O.C_3H_5O)\ (H)$ 77 73 73 1	— 113.7	— 268.3
Dimethyl propionylmalate $C(CH_2.CO.OCH_3)\ (CO.OCH_3)\ (O.C_3H_5O)\ (H)$ 73 59 73 1	— 22.9	— 50.0
Dipropyl isovalerylmalate $C(CH_2\ CO\ OC_3H_7)\ (CO.OC_3H_7)\ (O.C_5H_9O)\ (H)$ 101 87 101 1	— 21.7	— 65.5

2 A change in the order (transposition) of two group weights, which, according to the theory, should be accompanied by a change

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[1] Guye has introduced another constant of rotation in addition to the specific and molecular rotation, and expresses it by the formula

$$[\delta] = \frac{a}{l} \sqrt[3]{\frac{M}{d}},$$

in which α is the observed angle of rotation, l the length of column, M the molecular weight, and d the density of the substance Aignan criticized the applicability of the formula (Compt rend., **120**, 723)

[2] Le Bel Compt rend, **114**, 304, **119**, 226 Bull Soc Chim, [3], **7**, 613, 801 Colson: Compt rend., **114**, 175, 417, **115**, 729, 948, **116**, 319, 818, **119**, 65, **120**, 1416 Bull. Soc Chim, [3], **7**, 802, **9**, 1, 87, 195 Friedel Compt. rend **115**, 763, 994; **116**, 351 Freundler Compt. rend, **115**, 509, 866, **117**, 556 Bull Soc Chim., [3], **7**, 804, **9**, 409, 680; **11**, 305, 366, 468, 470, 477. Ann chim. phys [7], **3**, 487 Simon · Bull Soc. Chim, [3], **11**, 760 Purdie and Walker J Chem Soc, **63**, 240 Frankland and MacGregor. J Chem. Soc., **63**, 1416, 1430, **65**, 750 Piutti Gazz chim, **24**, II, 85. Binz · Ztschr. phys. Chem, **12**, 733 Goldschmidt Ztschr phys. Chem., **14**, 394 Wallach: Ann Chem. (Liebig), **276**, 316, 322

[3] Walden: Ztschr. phys. Chem., **15**, 638; **17**, 245, 705

[4] Walden: Ztschr. phys Chem., **17**, 245, 712 (1895).

in the direction of rotation, often is not followed by this effect.—Thus, we have according to Walden:[1]

Substance.	Order of the weights of the groups	Direction of rotation of the substance	Sign of the product of asymmetry
Mandelic acid $C(C_6H_5)(CO.OH)(OH)(H)$ 77 45 17 1	*a b c d*	+	+
Amyl mandelate $C(C_6H_5)(CO.OC_5H_{11})(OH)(H)$ 77 115 17 1	*b a c d*	+	—
Acetylmandelic acid $C(C_6H_5)(CO\ OH)(O.C_2H_3O)(H)$ 77 45 59 1	*a c b d*	+	—
Dipropyl acetylmalate $C(CH_2.CO.OC_3H_7)(CO.OC_3H_7)(O.C_2H_3O)(H)$ 101 87 59 1	*a b c d*	+	+
Dipropyl chloracetylmalate $C(CH_2.CO.OC_3H_7)(CO.OC_3H_7)(O.C_2H_2ClO)(H)$ 101 87 93.5 (1)	*a c b d*	+	—

On the other hand, by transposition of the group weights a change may follow in the direction of rotation, while the sign of the product of asymmetry remains the same. For example:

Substance.	Order of the weights of the groups.	Direction of rotation of the substance	Sign of the product of asymmetry
Mandelic acid $C(C_6H_5)(CO.OH)(OH)(H)$ 77 45 17 1	*a b c d*	+	+
Phenylbromacetic acid $C(C_6H_5)(CO.OH)(Br)(H)$ 77 45 80 1	*c a b d*	—	+
Phenylbromacetyl bromide $C(C_6H_5)(CO.Br)(Br)(H)$ 77 108 80 1	*b c a d*	—	+
Dimethyl malate $C(CH_2.CO.OCH_3)(CO.OCH_3)(OH)(H)$ 73 59 17 1	*a b c d*	+	+
Dimethyl bromsuccinate $C(CH_2.CO.OCH_3)(CO.OCH_3)(Br)(H)$ 73 59 80 1	*c a b d*	—	+

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[1] Walden: Ztschr. phys. Chem., 17, 705. The compounds were made from *l*-mandelic acid and had, therefore, a direction of rotation the opposite from that given in the table The same is true of the ester of malic acid.

3. In homologous series the changes in rotatory power and product of asymmetry are not parallel in the majority of cases, but subject to manifold deviations.

From all these considerations it has become evident that the principles on which the product of asymmetry is based, are not satisfactory It is clear, as Guye[1] also admits, that it is not alone the masses of the four groups which exert the influence, but also their relative positions, the actions which they have on each other, their configurations, and finally the nature of the elements themselves which are important in determining the direction and extent of rotation. On account of this complexity in the phenomenon, it is unlikely that, even through other means, will it ever be found possible to discover the numerical relations between amount of rotation and atomic structure of the molecule.

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[1] Guye and Chavanne Bull Soc Chim , [3], **15**, 195 (1895) Arch phys nat , [4], **1**, 54 (1896)

PART FOURTH

Apparatus and Methods for Determination of the Specific Rotation

87. General Conditions.—In the calculation of the specific rotation, the experimental determination of the following data is necessary :

1. The measurement of the angle of rotation α for a definite light ray.
2. The measurement of the length l of the tube for the liquid, in decimeters
3. The determination of the amount p of active substance in 100 grams of solution.
4. The determination of the specific gravity d of th solution.
5. The determination of the amount c of active substanc in 100 cubic centimeters of solution.

A. MEASUREMENT OF THE ANGLE OF ROTATION

88. Ordinary and Polarized Light.—While in an ordinary ligh ray the vibrations of the ether particles take place in al directions in a plane perpendicular to the line of propagation o the light, in a ray of plane polarized light the vibrations of th ether particles occur in a single direction only Such a plan polarized ray is no longer symmetrically disposed around it axis. The plane in which the ray is polarized is known as it *plane of polarization.*

The conversion of ordinary light into polarized light ma be effected, to begin with, by reflection, which is accomplishe by aid of the apparatus shown in Fig. 22. If a pencil of ligh be allowed to strike the black glass mirror A under an ang of 57°, the rays will be reflected upwards and *polarized in t* *plane of incidence.* The proof of this may be given by aid of the second mirror B. The reflected rays first pass through the empty vessel F, the bottom of which is formed of a plate of plane glass, and strike the mirror B under the same incident angle of 57°. By means of the lever D and the rack-work at E, B and the paper screen C may be rotated around a vertical axis. If the mirror B has a position parallel to A, the plane of incidence of the polarized rays reaching B coincides with their plane of polarization, and in consequence there is a considerable reflection toward C where a bright spot is formed by the pencil of light. On rotating the mirror B, however, the intensity of the light reflected from it gradually decreases until a position is reached 90° from the original one, when it is found that no more light is reflected and the screen C remains perfectly dark.[1] The plane of incidence of the rays

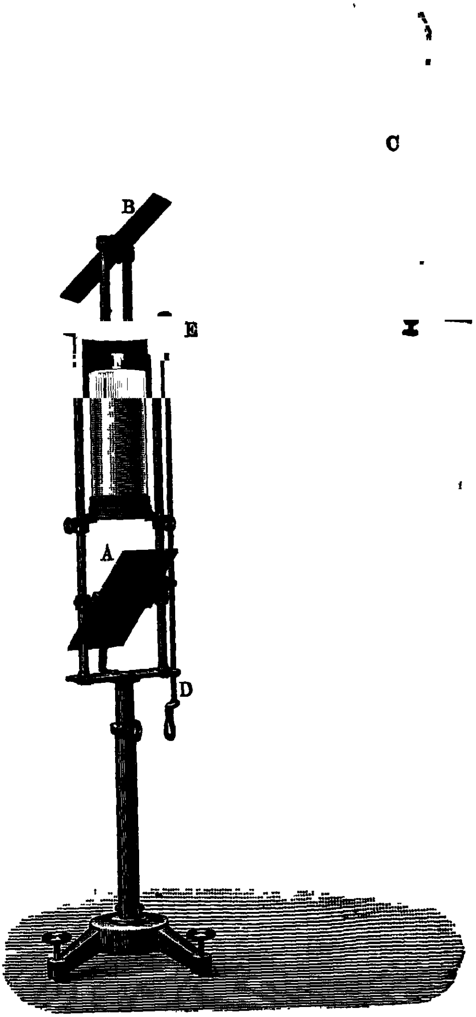

Fig 22.

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[1] All of the light is refracted in the glass and absorbed by the dark back surface.

is now perpendicular to the plane of polarization. On further rotation of the mirror B, it is found that at 180°, that is, in the position where the planes of incidence and polarization again coincide at B, there is a maximum and at 270° a minimum again of reflection.

89. **Rotation of the Plane of Polarization.**—Let the mirror B be brought into the position of greatest darkness, so that the plane of incidence of the rays polarized by the mirror A, and reaching B, is vertical to the new plane of polarization. If the vessel F be now filled with a cane-sugar solution, for example, the remarkable phenomenon is exhibited in which the screen C becomes suddenly bright and remains so until the mirror B is rotated through a certain angle. Now, again, as a matter of course, the plane of incidence of the transmitted rays is perpendicular to their plane of polarization. It follows, therefore, that the plane of polarization of the rays reflected through the sugar solution has been turned or twisted through an angle equal to that through which B was turned. This angle is known as the *angle of rotation.*

90. **Iceland Spar Prisms.**—A pencil of light may be linearly polarized by double refraction in crystals, especially in Iceland spar, much more perfectly than by reflection. If a ray of light falls perpendicularly on one of the faces of a natural Iceland spar rhombohedron it is broken up, on entering the crystal, into two separate rays, unequally refracted and linearly polarized in planes perpendicular to each other. If we define as the *optical axis* of the crystal that direction parallel to which no double refraction and also no polarization takes place, and as the *optical principal plane* of the incident ray, that plane which includes the perpendicular at the point of incidence and also the optical axis, then the principal plane is at the same time the plane of polarization of the ordinary refracted ray, while the plane of polarization of the extraordinary ray is perpendicular to the principal plane. This holds still accurately true when the incident ray instead of falling vertically upon the surface of the crystal strikes it at any angle, as long as the incident plane is at the same time a principal plane of the crystal. In the practical applications of these rays in polar-

ization instruments it is better to permit only one to emerge, in the direction of the incident light, while the other is eliminated. This may be accomplished in various ways, most perfectly on converting the Iceland spar into a Nicol prism. The polarization prisms,[1] described at length below, are used in the modern forms of polarization instruments for scientific as well as for technical purposes.

1. *Nicol's Prism*—This, which is the most widely known type, is made in the following manner: A rhombohedron, *a b c d* (Fig. 23), the length of which is fully three times the width, is cut from a clear crystal of Iceland spar; the end surfaces, which make originally angles of 71° with the side edges, are polished off so that these angles, at *a* and *c*, become 68°, and then the prism is sawed through in the direction *b'*, *d'*. After the angles *a b' d'* and *c d' b'* are ground down to 90° and the sawed surfaces polished they are cemented together again in the original position by means of Canada balsam Finally the side surfaces are blackened and the finished nicol is fastened into a brass frame by aid of cork The optical principal plane of the prism for all rays falling on the ends is the plane vertical to the end surfaces and passing through the optical axis.

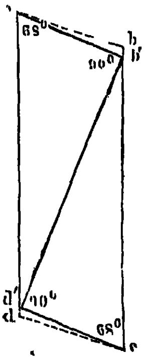

Fig 23

In illustration, if a ray of light whose plane of incidence contains the optical axis falls upon one of the end surfaces, it is divided on entering into two rays polarized perpendicularly to each other In case the entering ray makes but a small angle with the axis of length of the prism, the ordinary component suffers total reflection on the cement surface, is thrown to the dark side surface and is here largely absorbed, while the extraordinary component passes through the cement and emerges alone from the second end surface in a direction parallel to that of entrance. The plane of polarization of this emerging ray is vertical to the principal plane.

If a small flame at some distance is observed through the nicol, under such condition that the entering rays make but a small angle with the axis of length of the prism, the eye perceives uniform illumination within a certain limited field, and the planes of polarization of the individual linearly polarized rays coming through the prism deviate very little from each other, that is, within certain limits, they are all polarized perpendicularly to the principal section of the nicol. It may then be briefly said (although not with absolute accuracy) that when a pencil of light passes through a nicol, the emerging light is linearly polarized, and in a direction vertical to the principal section.[1]

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[1] Feussner: "Ueber die Prismen zur Polarisation des Lichtes," Ztschr f Instrum., 4, 41 (1884). Grosse "Ueber Polarisationsprismen," Ztschr f Instrum, 10, 445 (1890). Halle: "Ueber Herstellung Nicol'scher Prismen," V d. D Ges f Mech u Opt, 143 (1896).

The plane of polarization of the light emerging from a nicol can be found most simply, empirically, by aid of a revolving glass mirror. The light from the prism is allowed to strike the mirror under an incident angle of 57°, and the glass is then rotated around the rays as an axis until all reflected light disappears. According to § 88 the plane of polarization of the nicol is now vertical to the incident plane of the rays on the mirror.

2. *Hartnack-Prazmowski Prism* —From the natural crystal, a b c d (Fig. 24), the prism a′ b′ c′ d′ is cut out and sawed in the direction a′ c′. After the surfaces a′ b′ and c′ d′ and the sawed surfaces a′ c′ are ground and polished the latter are cemented together. The entering angle b′ a′ c′ must vary according as Canada balsam, linseed oil or other transparent cement is employed. Although the loss of material on cutting the crystal is greater than in the Nicol prism, the Hartnack prism possesses, notwithstanding its shorter length, a much greater field of view. Besides this, it has the advantage of presenting straight end surfaces. In the prism, as described by Hartnack, the optical axis stands vertical to the plane of the section a′ c′; the optical principal section is, therefore, a plane through the axis of length and vertical to the cut surface.

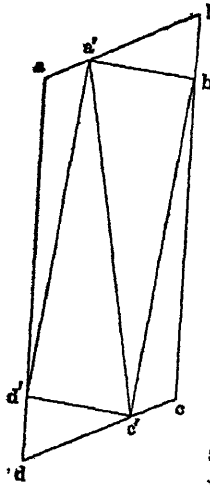

Fig. 24

3. *Prism of Glan* [-Thompson].[2]—A much greater loss of

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[1] For further details see Lippich · "Ueber polaristrobometrische Methoden, Wien. Sitzungsber. II, 85, 268 (1882)

[2] Lippich has constructed a similar prism. Wien, Sitzungsber. II, 91, 1079. (1885). The Glan prism with air layer is not to be confounded with the above.

material than in the last prism is suffered in that of Glan. On a symmetrical rhombohedral crystal, two surfaces are ground down parallel to each other and perpendicular to the optical axis of the crystal A B C (Fig 25); vertically to these surfaces the prism a b c d is then cut out and sawed through in the direction b d. After the surfaces a b and c d, and the cut faces b d are ground and polished, the two halves are cemented together. The angle a b d depends, as before, on the kind of cement which is employed.

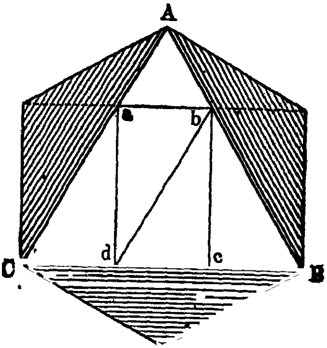

Fig 25

The Glan prism surpasses the others described in having an essentially larger opening with corresponding length, the field of view is also normal to and symmetrical with the axis of length of the prism. This prism may therefore be described as scientifically the most perfect form, and for this reason it has come into use as the polarizing prism in all good instruments. As the optical axis of the prism is adjusted parallel to the refractive edges b and d of the piece of spar, it follows that the optical principal section is a plane through the axis of length and vertical to the edge a b.

91. **Polarizer and Analyzer.**—If ordinary light from any source is passed through a nicol the emerging light, as explained in the last paragraph, is linearly polarized perpendicularly to the principal section. Such a linearly polarized ray may be decomposed, like a force, into two linearly polarized components, vertical to each other as regards their planes of polarization If then linearly polarized light, the plane of polarization and amplitude of which is A B (Fig 26), falls on a new Nicol, the principal section C D of which makes an angle α with A B, this light may be broken up into two components, A E $=$ A B $\cos \alpha$ and A F $=$ A B $\sin \alpha$. Only the latter component, which is perpendicular to the principal section, will pass

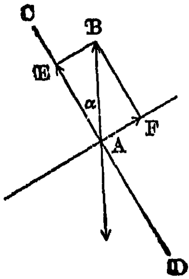

Fig. 26.

through, while the component A E, which is polarized in the principal section, is completely extinguished by the nicol. Of a linearly polarized light ray only that component can pass a Nicol prism which is perpendicular to the principal section, and this component is the smaller the smaller the angle which the plane of polarization of the entering ray makes with the principal section of the nicol If now the nicol is rotated all light passes when C D is brought perpendicular to A B; on further turning, the light passing becomes gradually weaker, and after reaching 90° (C D parallel with A B) complete darkness follows. On still further turning, the light reappears and reaches a maximum of brightness at 180°, and so on.

Let the following conditions be considered: We place two Nicol prisms between the eye and a small luminous surface at some distance, and one before the other in such position that their principal sections are parallel with the line of vision. The nicol nearest the light may be in fixed position while the one next the eye may be rotated around its axis of length. The first one is called the *polarizer* and the other the *analyzer* The light reaching the polarizer from the luminous surface is, after passage, linearly polarized vertically to the principal section. This next reaches the analyzer If this is at first turned so that its principal section is parallel with that of the polarizer, the already polarized light suffers no further change in passing through the analyzer, and the eye perceives the field of view brightly illuminated. This is also the case when the analyzer is turned through 180°, which brings the principal sections into parallel position again. If, next, the analyzer be so placed that its principal section crosses that of the polarizer at right angles the polarized light will be completely shut off, because now its plane of polarization and the principal section of the analyzer coincide. The rays entering the analyzer behave as *ordinary* polarized rays until the cement layer is reached and here they are thrown off by reflection. No light can, therefore, pass the analyzer and the field of view remains dark. The same is true after rotating 180°. In all other cases in which the principal sections of the two nicols are neither parallel nor vertical, a part of the light entering the analyzer will be allowed to pass, and always that component which is polarized perpendicularly to the principal section of the analyzer.

92. Polarization Apparatus.—The apparatus shown in Fig. 27 may be used for the observation of these phenomena. The horizontal bar d, supported on a stand, carries at one end the polarizing Nicol, a, in fixed position, and at the other the analyzer b, which may be turned with its receptacle, by means of the lever c, around its axis. A single or double pointer is turned with it over the graduated circle fastened also to the bar, d Between the Nicols the tube, f, may be placed, the ends of which are closed by glass plates.

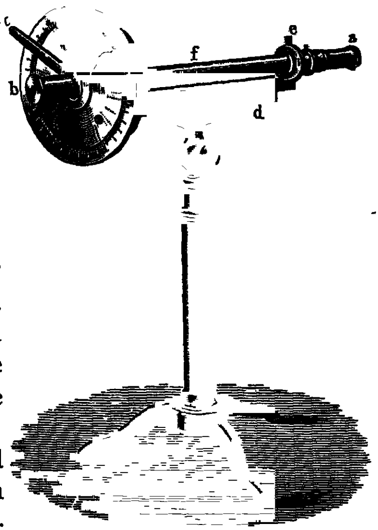

Fig 27

The polarizer is first turned toward a source of light, which for the sake of greater simplicity in the phenomenon should be monochromatic, such as given, for example, by a Bunsen burner and sodium carbonate bead. At first the tube remains empty. On looking through the analyzer and rotating it, a position is easily found in which the field appears at its greatest darkness Assuming that the pointer is now at 0° on the circle, from what was said above it will appear that the second position of darkness will be at 180°, and the two brightest positions at 90° and 270°. For the observations, the darker positions are more suitable than the light ones, because with the former a small motion of the nicol makes a very perceptible change.

The position of the analyzer at which the field has the greatest darkness, is called the *zero point of the apparatus.* In this position the plane of polarization of the light coming from the polarizer coincides with the principal section of the analyzer. If now the tube f be filled with a cane-sugar solution and placed in the apparatus, the plane of polarization of the light coming from the polarizer will undergo rotation through a certain angle, α, by action of the sugar solution as explained above. In consequence of this, the field of view becomes bright. Darkness will come again when the principal section of the analyzer is brought into parallel position with the rotated plane of polarization; that is, when the analyzer, also, is turned through the angle α. This angle α may be read off on the graduated circle and is equal to the angle of rotation of the sugar solution. If after putting an optically active substance in the tube, it is necessary to turn the analyzer from 0 in the direction of the clock-hand motion to reach the point again where the light disappears, the substance is said to be *right rotating;* if the analyzer is turned in the opposite direction to reach the same end, the substance is *left-rotating*.

93. **Determination of the Direction and Angle of Rotation.**—With exception of the Wild polaristrobometer, which has four zero points, all polarization instruments have two zero points 180° apart. We assume, first, that we have to do with one of the latter forms. By the aid of such apparatus we have to determine the direction of rotation, and the amount of rotation of an active substance. After adjusting the apparatus to the zero point and putting the active substance in position, the analyzer must be turned say, through $+\alpha^\circ$ (α certainly less than 180°), that is, in the clock-hand direction, to darken the field again. The angle α read off is not yet necessarily the angle of rotation; as regards whole multiples of $\pm$ 180° it is yet quite undetermined. It can only be said that the angle of rotation of the substance is equal to $\alpha^\circ \pm n\ 180^\circ$, where n is either 0 or a whole number to be determined. In the case of a solid substance, if the thickness of the layer is not above a few millimeters, or in the case of a liquid if the tube length is not above two decimeters, then, unless the substance is one possessing unusually great activity, the angle of rotation will be less than 180°, so that the choice will lie between $+\alpha^\circ$ and $+\alpha^\circ - 180^\circ$. In order to decide between these two angles the same substance must be examined in a layer of just one-half the thickness, or, in the case of solutions, one of just half the concentration, with the same tube length, may be employed; now the angle of rotation will be half as great as before. Suppose the angle is now $+\beta$, a simple consideration will show

this · If $\beta = \frac{\alpha}{2}$ the substance is right rotating with an angle of α for the full thickness of layer. If $\beta = 90° + \frac{\alpha}{2}$ then the substance is left rotating with an angle of rotation equal to $\alpha° - 180°$ for the full thickness of layer.

The direction of rotation of a liquid may be very conveniently found by filling it into the control observation tube, with variable length, of Schmidt and Haensch, to be later described After putting the tube in place the analyzer is moved to the position of darkness; the tube is then lengthened a little, which produces a brightening of the field. If it is now necessary to turn the analyzer a few degrees in the clock motion direction to secure darkness again, the liquid is right rotating; but, on the other hand, if the analyzer must be turned in the opposite direction the liquid is left-rotating.

The determination of the direction and amount of rotation by aid of the Wild instrument is more complicated, because this possesses four zero points 90° apart. Under the assumption that the angle of rotation is less than ± 90°, the direction and number of degrees of rotation may be found by a plan similar to that just outlined, by working first with a layer of full length and then with one of half the length. But if angles up to ± 180° are possible then a third length of layer of substance must be taken which is one-fourth the first length. Here also the application of the Schmidt and Haensch control observation tube would be advantageous, the length being first contracted to one-half and then to one-fourth. The position of the Nicol is then always observed in the first quadrant, between 0° and 90°, and the graduation on the circle follows in this manner, that in the case of a small right-rotation of the plane of polarization, with observations in the first quadrant, small numbers close to the 0 are read off. The correctness of the following can then be easily demonstrated; if the reading with full thickness of layer is $\alpha°$, and if further, with one-fourth this thickness, it is

$= \frac{\alpha}{4}$, then substance is right rotating with the angle $\alpha°$,

$= 22.5 + \frac{\alpha}{4}$, then substance is right rotating with the angle $90° + \alpha°$,

$= 45 \quad + \frac{\alpha}{4}$, then substance is left rotating with the angle $180° - \alpha°$,

$= 67.5 + \frac{\alpha}{4}$, then substance is left rotating with the angle $90° - \alpha°$;

Here the angles α, $90° + \alpha$, $180° - \alpha$, $90° - \alpha$ refer to the full thickness of layer.

a. Polarization Instruments

94. **Polarization Apparatus and Saccharimeters.**—For the exact measurement of the angle of rotation different instruments have been constructed, which, according to their uses, are divided into two classes. These are:

1. The so-called *Polariscopes* or *Polaristrobometers*.—These are used for scientific purposes in the investigation of all active substances. They have a circular graduation and require homogeneous light.

2. *The Saccharimeters.*—These are specially constructed for the determination of the strength of sugar solutions. In place of the circular graduation, they have a quartz wedge compensation with linear scale and employ white light. They are used chiefly in the sugar industry.

95. **Construction of the Polariscopes.**—Before taking up the description of the special forms of instruments, a short discussion of the requirements in a good polariscope will be given, and also an explanation of the path of the light rays through the apparatus[1] The following considerations obtain for all polariscopes and saccharimeters, with the exception of the Wild instrument, which, in principle, is different from all other forms of apparatus.

Those optical parts which all polarization instruments have, in common, are shown in Fig. 28. The light from the luminous body A passes through the lens B into the instrument and is linearly polarized by the polarizer C. Immediately in front of this is found the round polarizer diaphragm D, which is focused on. Then follow the round analyzer diaphragm E, the analyzer F, and a reading telescope. In the figure an ordinary astronomical telescope is shown with the objective G, the ocular H, and the diaphragm J, in front of which the eye of the observer is placed. At the outset, the parts from B to J must be accurately adjusted with reference to the axis of the instrument. Inasmuch, as we shall presently see, as all light going through the instrument is limited by the diaphragms D and E, at any rate in the forms as now commonly constructed, and as all bodies to be investigated with reference to their rotating power are placed between D and E we shall understand as the *axis of the apparatus* from now on, the line which unites the centers of the diaphragms D and E. All other optical parts of the instrument must be exactly centered on this line Although the adjustment of the illuminating lens B need be only approximately correct, the polarizer C must be so centered that its optical principal section is exactly parallel to this axis of the instrument. As regards the size of the diaphragms D and E, these must be correspondingly smaller than the cross dimensions of the prisms C and F, so that a sufficiently broad border of about two millimeters in diameter around the edges of the prisms should be obscured.

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[1] See, also Lippich: Wien. Sitzungsber., II, 85, 268 (1882); 91, 1059 (1885). These considerations on the construction of apparatus and the path of the light rays should be carefully followed, in all more exact work, if one wishes to be certain of excluding bad systematic errors in the results.

While in the case of the saccharimeters all the optical parts are fixed with exception of the ocular H J, which is movable in the direction of the axis, in the polariscopes the parts E to J may be rotated around a common axis. This axis of rotation, which at most should not be inclined more than a few minutes, must coincide exactly with the axis of the apparatus. This may be easily secured in the smaller forms of apparatus, which, like the saccharimeters, can be worked out in the lathe, but is realized with greater difficulty in the larger instruments, which are composed of the distinct parts B to D and E to J. It may hap-

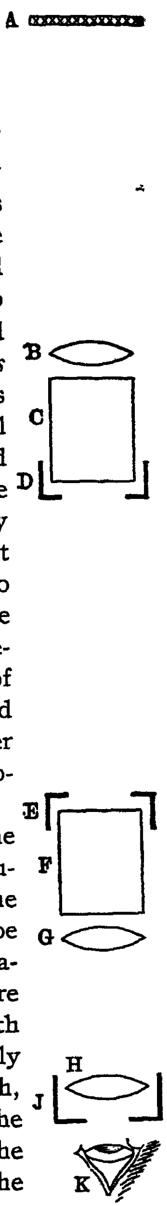

Fig. 28.

pen here, that, in instruments most excellent in all other respects, the inclination of the axis of rotation with reference to the axis of the apparatus may amount to as much as ten minutes or even more. In order to avoid such an error the diaphragm D must be attached after the other parts of the apparatus are fastened to the support, and then, if necessary, eccentrically with reference to the thread. The optical principal section of the analyzer F must be exactly parallel to the axis of the apparatus and the axis of rotation, while the requirement that the axis of rotation must be at the same time the optical axis of the telescope G H J, is one which can always be met satisfactorily.

But, above all, care must be taken to have the adjustment of the prisms C and F, with reference to each other, a fixed and unchangeable one, as otherwise constant variations in the zero point would result. With the saccharimeters, therefore, the prism must be fixed once for all, and in the polariscopes the optical principal section of the rotating analyzer must remain always parallel to the axis of the instrument. We have the following two criteria by which to determine whether or not the prisms in the polariscope are properly adjusted and free from errors. *First, the two zero points of the apparatus must be exactly 180° apart; second, if a large angle, say 90°, is measured, the two final observation readings 180° apart must give exactly the same value for the angle of rotation.*

While with the smaller polariscopes the graduated circle generally remains at rest with the rotation of the analyzer, and the verniers only move, in the larger instruments the graduated circle rotates with the analyzer. In order to eliminate the unavoidable errors of graduation in the circle, the analyzer is furnished with a setting which may be rotated independently, or the shell to which the verniers are attached may be turned through 360°, which is easily done. *In this way the zero point of the apparatus may be brought to correspond to any part of the circle, and the rotation, therefore, measured with different parts of the graduation.* In order to eliminate the eccentricity of the circle, that is, the error, which is due to the fact that the axis of rotation does not pass exactly through the center of the disk, two observation verniers, 180° apart, are always attached. Both of these must be read each time and the mean of the angles, as given by each vernier, taken; of course, with the double reading the error of observation, also, is reduced. Besides, the plane of the graduated circle must be vertical to the axis of rotation, otherwise, different values for the same angle of rotation would be found on different parts of the graduation. But such an error is not greatly to be feared, as it is not a difficult matter for the instrument-maker to fulfil this requirement in a satisfactory manner.

96. **Path of the Rays in the Polariscope.**—If one wishes to secure, in reality, the remarkable accuracy which may be reached in the best forms of polariscopes, it is, above all, necessary to provide for a *perfectly correct course* of the rays through the instrument to the eye of the observer In all accurate polariscopes or saccharimeters, the observer focuses on a field which is made up of two or more separate fields, the illuminations of which are compared with each other. If full advantage is taken of the delicacy of this method of reading, the brightness of each separate field must be perfectly uniform, and second, with the apparatus at rest, the degree of illumination on the several fields must remain absolutely constant, or, expressed differently, *the distribution of the illumination in the whole field of view must remain always uniform* Both conditions could easily be reached if the source of light were uniform in intensity throughout. This is, however, never absolutely the case, and it must then be *determined how the rays may be passed through the apparatus in order that the two requirements mentioned may be satisfied, notwithstanding changes and irregularities in the distribution of the luminosity of the source of light itself* It must be assumed, however, that every point in the source of light illuminates equally in all directions. This condition will always obtain, if the small surface of the illuminating lens, and only such can be considered here, is kept at a relatively great distance from the source of light, and this will be assumed in what is to come.

In order to simplify the following discussion let us imagine first the two polarization prisms C and F of Fig. 28 removed and the two diphragms D and E brought close to the two lenses B and G, so that we have essentially only the luminous

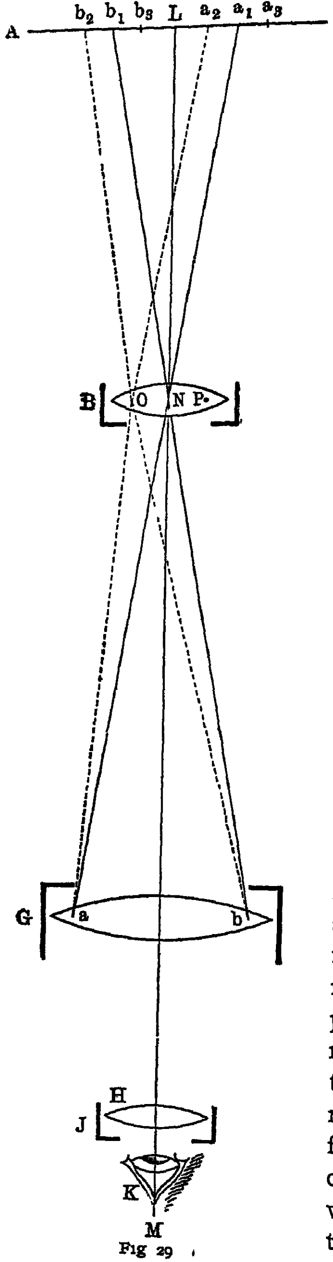

Fig 29

surface A (Fig. 29), the illuminating lens B, which is now focused on, and the telescope G H J left. We shall consider first the path of the rays in the case in which the *polarization prisms are placed in parallel light rays.* In order to realize this condition we must choose an illumination lens of long focus and place the luminous body in its focal plane. A is, therefore, in the focal plane of the lens B. Let L M represent the axis of the apparatus The degree of brightness under which an element of surface at the point N of the illuminating lens is seen, depends on the cone of rays a N b, supposing the luminous surface at A large enough to begin with, and that all the rays in the cone a N b actually pass through the reading telescope and reach the eye of the observer. Since all the rays in the cone a N b were, before passing the lens B, in the cone a_1 N b_1, therefore the brightness at N is proportional to the amount of light which is sent out from the part a_1 b_1 of the luminous surface If we consider a point at O, near the edge of B, its brightness is determined by the cone a O b Remembering now that A is situated in the focal plane of B it follows that corresponding to the cone a O b we have, before passing the lens, the cone a_2 O b_2, in which, for example, a O is parallel with a_2 N. The brightness at O is proportional, therefore, to the amount of light emitted from a_2 b_2 of the luminous body. In the same manner the brightness at P, a point symmetrical with O, is proportional to the light emitted from the part a_3 b_3 of the luminous body. We see, therefore, that for every point of B, the corresponding part a_n b_n embraces a different portion of the luminous body. It follows, therefore, that unless the area b_2 a_3 of the luminous body is uniform in brightness, the lens B cannot appear uniformly bright, and further that the distribution of the illumination at B, on account of changes in the luminous body, may be different at different times, but if the luminous surface is narrowed down to the portion b_3 a_2, the luminosity in every part of B is then proportional to the light emitted from b_3 a_2 Now, whatever the distribution of the light may be in the part b_3 a_2, the lens B will appear uniformly bright, as in principle it is required to be.

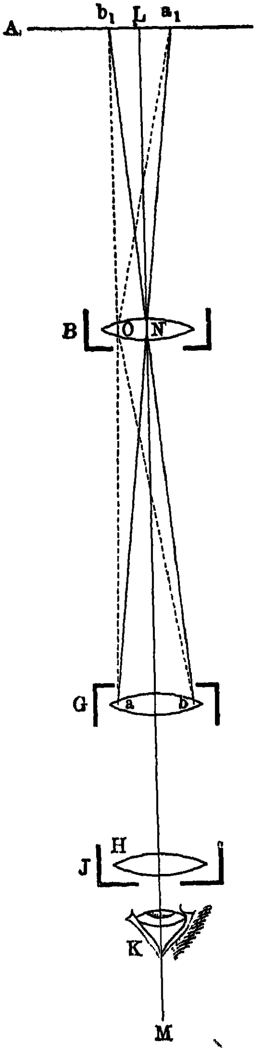

Fig. 30.

If the diameter of the diaphragm B is represented by d_1, and that of the diaphragm G by d_2, the distance between the two diaphragms by c and the focal distance of the lens B by f, a simple examination shows that the diameter e, of the diaphragm in front of the light, that is b_3 a_2, is determined by the expression, $e = f\,(d_2 - d_1) \div c$. If then, the lens B is to appear uniformly bright, the objective G must be so chosen as to be larger than the field of view on B, and care must also be taken to shut out so much of the light by means of a diaphragm that the luminous disk remaining is smaller than $f(d_2 - d_1) - c$.

Essentially simpler and more favorable are the conditions when the polarization prisms are placed in convergent light. In Fig 30 let A again represent the luminous surface, B the illumination lens to be focused on, and G H J the reading telescope We give the light A such a position that its image is produced through B at G, which may always be easily done by properly choosing B Then the brightness of the point N on the illumination lens is determined by the cone a N b, equivalent to $a_1 N b_1$. The brightness of N is thus proportional to the amount of light emitted by a_1 b_1 If we consider another point O on the lens, its illumination will be determined by a O b This corresponds to $a_1 O b_1$ as a b is the image of a_1 b_1 The brightness at O is, therefore, also proportional to the light emitted by a_1 b_1 Each point on B consequently receives its light from the part a_1 b_1 of the luminous surface, so that the lens B appears uniformly illuminated, however the distribution of the luminosity in the source of light may be changed. If any part of a_1 b_1 be shut off by a screen, the total illumination of the field of view, B, will be decreased, but the uniformity of the light will remain undisturbed. It may be looked upon then as an important rule which should always be followed, that the source of light should be given such a position that its image may be thrown upon the telescope objective by the illumination lens B

In the forms of apparatus now common, the entering light rays are not limited by the diaphragms of the illumination and telescope objective lenses, but by the polarizer and analyzer diaphragms, and it is the polarizer diaphragm which is focused on, and which therefore must appear uniformly illuminated. This will always be the case, as may now be readily understood, if the *source of light is given such a position that its image, through the illumination lens, is thrown on the analyzer diaphragm,*[1] it being understood, of course, that none of the ray bundles appearing between the polarizer and analyzer diaphragms, if followed back to the light or forward to the eye, suffer a partial interruption As may be shown easily, the diaphragm l of the illumination lens must be taken greater than $(gi + gk + hk) \div i$, and on the other hand, the diaphragm n of the telescope objective must be larger than $(hi + hm + gm) \div i$, where g represents the diameter of the polarizer diaphragm, h the diameter of the analyzer diaphragm, i the distance between polarizer and analyzer diaphragms, k the distance between polarizer diaphragm and illumination lens, and m, finally, the distance between the analyzer diaphragm and telescope objective. As may be seen, the polarizer and analyzer diaphragms may have the same or different openings ; but, it is preferable not to make the polarizer diaphragm too small, as the sensitiveness of the readings becomes less with smaller field of view, and to take the analyzer diaphragm as large as possible, as the brightness of the field increases with its size. As regards the focal length of the illumination lens it is desirable to produce a full-sized image of the source of light with it, and this focal length should be, therefore, equal to half the distance between it and the analyzer diaphragm, with the light placed at a distance from the illumination lens equal to the distance between the latter and the analyzer diaphragm. It is always good to place a screen immediately in front of the light, and to choose its size so that the image of the opening in this screen on the analyzer diaphragm is a little larger than this diaphragm.

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[1] To determine this, hold a piece of white paper over the analyzer diaphragm and a pointed wire just in front of the source of light; then the light, with the wire, is given such a position that a sharp image of the point is produced on the paper at the diaphragm opening.

If the diameter n of the telescope objective is taken large enough, all the rays coming from the analyzer diaphragm will pass through it, and it only remains to provide that these rays actually reach the pupil of the observer's eye, as the two diaphragms of the ocular and eye-piece cap may always be chosen large enough. In order to secure the first it is simplest to arrange the construction so that the *pupil may be brought exactly in the plane of the ocular circle*, *or*, *more accurately stated*, *in the plane of the image of the analyzer diaphragm produced by the telescope.* By rightly choosing the magnification it is easily possible to keep the ocular circle within a diameter of about 4 mm , so that all rays may pass through the pupil. But it is not even necessary to keep the ocular circle smaller than the pupil, because the shutting off of the part of the circle outside of the edge of the pupil will not alter in any manner the distribution of the illumination as it appears on the polarizer diaphragm, since the ocular circle is the image of the analyzer diaphragm, and therefore, at the same time, the image of the source of light. A part of the light may, therefore, be screened off by the pupil, which, as explained above, decreases the total intensity of illumination of the field, but does not change its uniformity. But in order to keep the field of view as bright as possible, it is always preferable to keep the ocular circle smaller than the pupil. It follows also that *as long as the pupil is kept in the plane of the ocular circle, changes in the position of the eye may be as great as desirable without altering the uniform distribution of illumination of the field of view* But the case is quite different if the pupil is not brought into the plane of the ocular circle, because now the bundles of rays from different parts of the field of view may be unevenly screened or obscured by the pupil, in consequence of which the illumination of the field may no longer appear uniform. Therefore only astronomical telescopes with convergent oculars may be used, while the ordinary Galilean telescope, in which the ocular circle lies within the instrument, should be avoided; commonly a magnification of four to six diameters is chosen In order to be able to bring the pupil with certainty within the plane of the ocular circle, the eyepiece cap must be always so attached that the circle is formed a little beyond it; the pupil will then lie in the ocular circle plane when the eye is held pretty close to the eyepiece cap

If in this way a perfectly normal path of the light rays through the apparatus and to the eye of the observer is provided for, no zero point or observation errors will be occasioned by changes in the illumination flame or by deviations in the rays themselves. It has thus far been assumed that no rotating substance is in the apparatus, which is the case in the zero point adjustment. But if this condition is not true, as, for example, when a substance with refractive index greater than that of the air is present in appreciable length (a filled tube), then the course of the rays as outlined will no longer exactly hold true. In order to focus the telescope sharply on the polarizer diaphragm, the eyepiece must be adjusted again, and the image of the source of light will no longer be formed at the analyzer diaphragm. It may, however, be easily provided for that the path of the light shall remain perfectly correct when the zero point determination is made and also when a filled tube is in position, which question, however, will not be taken up in detail at this time.

The rotating substances and observation tubes must be perfectly centered with reference to the axis, and care should be taken to have the diaphragms on the observation tubes somewhat larger than the polarizer and analyzer diaphragms, in order that none of the light rays normally in the field of view may be screened off. Finally, it may be remembered that it is an error to place lenses, or glass vessels with absorbing liquids to purify the light, between the polarizer and analyzer.

97. **Making the Observation.**—In order to avoid repetitions in the descriptions of apparatus, the general method of carrying out an observation will be explained here Take first the case of measuring the angle of rotation of a substance with an instrument which has two zero points 180° apart. After the light is so arranged that a sharp image of the screen opening in front of it is thrown on the polarizer diaphragm by the illumination lens, the telescope is sharply focused on the polarizer diaphragm. By now rotating the analyzer several zero point observations are made at each side of the graduated circle, and in all more exact work both verniers should be always read off *After inserting the rotating substance the telescope is again sharply focused.* On again making a sufficient number of adjustments and readings on both verniers, and then more readings of the zero point after removal of the active substance, we obtain by subtraction a mean value of the angle of rotation from which the eccentricity of the graduated circle is eliminated. If now the observations are repeated, starting with the second zero point 180° from the first, the same angle of rotation should be found, provided the polarization prisms are properly constructed and centered, and the angle of rotation itself has not changed Otherwise the mean of the two values must be taken and this considered as the true angle of rotation. Between the different observations it is well also to rotate the substance or polarization tube in order

to compensate errors which may arise from imperfect parallelism in the end surfaces of the observed substance. With the Wild polaristrobometer one must naturally make readings, in all accurate work, in each of the four quadrants of the circle and then take the mean of the four angles so determined

If the rotation of a cane-sugar solution is to be found by the aid of a saccharimeter, the light is arranged, as before, so that a sharp image of the front screen is formed by the illuminating lens at the analyzer diaphragm. From the zero point reading and those made after placing the polarizing tube in position, the rotation is obtained by subtraction. Between readings the tube should be rotated around its axis In technical work where numerous observations are made, one after the other, a few readings are sufficient to secure exact results; it is also enough to determine the zero point every hour

In order to keep all outside light from the instrument the room should be at least partly darkened; and in general it may be said that the darker the room the greater is the accuracy in observation

α Older Forms of Apparatus.

1. Biot (Mitscherlich) Polariscope[1]

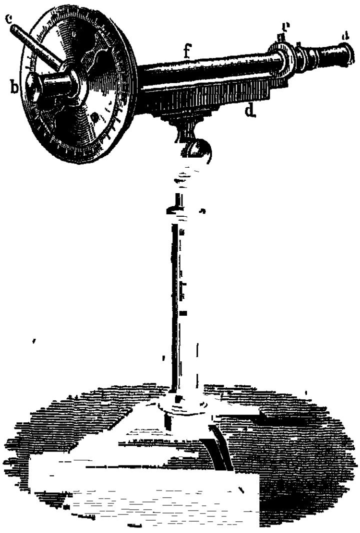

Fig 31

98. Description of the Instrument.—This, the simplest of all polaristrobometers, first made by Biot, and which was referred to in §92, consisted of a stand, polarizer, analyzer, and graduated circle Later, the polarizer was provided with a small circular diaphragm to which the eye was to be accommodated, and in order to increase the intensity of the illumination, a small double convex lens was added in front. The Mitscherlich apparatus is shown in Fig. 31. The two polarization prisms are attached at the ends of a horizontal bar of brass or wood. The polarizer and the illumination lens are found in a brass tube a, which may be rotated, if necessary, and then made fast by turning the small screw e. The supporting frame of the analyzer b, which may be rotated, is furnished with a handle, c, and two pointers, which have either a simple index mark or vernier, and which move over the fixed graduated circle The divisions are in degrees, and the readings may be made to tenths of a degree. The polarization tube may be laid in between the two prisms and has usually a length of 20 cm If the pointers are furnished with verniers, the alidades to the right and the left of the index zero are divided, so that 10 divisions on the scale equal 9° on the circle, which permits a direct reading to one-tenth degree In the adjoining Fig 32, the zero of the vernier does not quite reach the third degree mark on the circle, to the right, and the sixth vernier mark is the first one which makes a coincidence The alidade reading is, therefore, + 2 6° A further improvement in the Mitscherlich instrument was the addition of a small reading telescope in front of the analyzer.

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[1] Biot Ann chim phys, [2], 74, 401 (1840). Mitscherlich "Lehrbuch der Chemie," 4th ed, 1, 361 (1844).

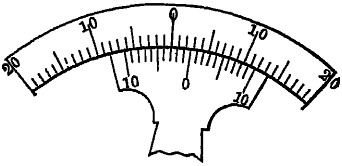

Fig 32

99. **Observation with Homogeneous Light.**—In the use of the apparatus it is preferable to employ homogeneous, yellow sodium light, and so find the rotation for the ray D. To find the zero point, the polarization tube is placed in position, either empty or filled with water, and then the analyzer is turned until the position of maximum darkness is reached If the round field of view is at all large, complete darkening of the whole field does not occur, but a black band is observed,[1] the edges of which grow gradually lighter (Fig 33), and this is brought as nearly as possible to the center of the field by moving the analyzer. On repeating this several times and taking the mean of the readings, the true zero point is found If it is desired

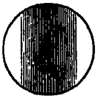

Fig 33

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[1] For the theory of this, see Lippich, "Ueber polaristrobometrische Methoden," Wien. Sitzungsber., II, 85, 268 (1882)

to have this coincide as nearly as possible with the zero of the graduation, which is not at all necessary, the index is first brought to zero, and then, after loosening the screw e (Fig. 31), the polarizer is turned until the black band appears in the middle. Ordinarily, this adjustment is carried out by the maker of the instrument.

If now the observation tube filled with the active liquid is placed in position the field of view appears bright again, and it is necessary to turn the analyzer through a certain angle, equal to the angle of rotation of the substance, to cause the reappearance of the dark band. This is repeated for the position 180° distant Concerning the observations and determination of direction of rotation see §93 and §97 The mean error in the readings is about ± 0.1°.

This form of apparatus is employed at the present time only in the determination of rotation dispersion.

2. *Robiquet's Polariscope*

100. **Description of the Instrument.**—Robiquet made the Mitscherlich apparatus much more sensitive by adding to the polarizer the double quartz plate, constructed by Soleil, the theory of which is given in the next paragraph. Robiquet's instrument is shown in Fig. 34. A brass trough with a section of half a circle, a b, which may be covered by a corre-

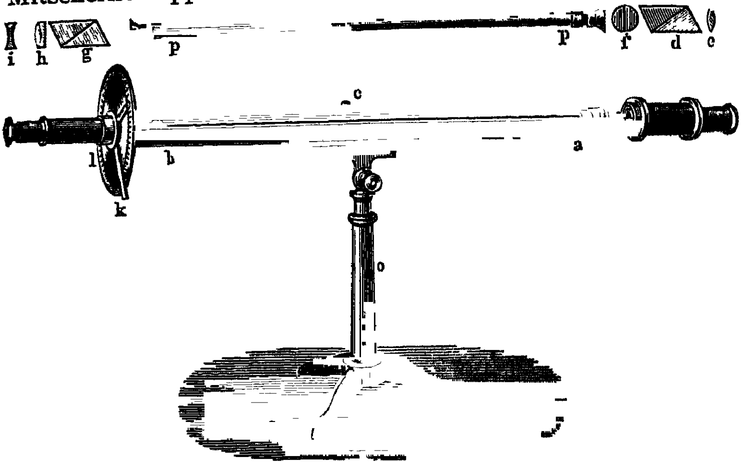

Fig 34

sponding lid, c, forming a tube, carries at one end in a fixed shell the polarizing Nicol, d. In front of this is the illumination lens e, and at the other side, at f, the Soleil double plate. At the other end of the trough is the rotating analyzer g, and a small Galilean telescope, consisting of the objective h and the ocular i. The analyzer is turned by aid of the lever k; the angle of rotation is read off on the graduated circle l. Glass tubes, p p, containing the liquid to be examined are laid in the trough. The whole is supported on the stand o.

101. **Theory of the Soleil Double Plate.**—The biquartz consists of two equally thick quartz plates, one of which is left rotating, the other right rotating, cut vertically to the optical axis and cemented together. The last grinding and polishing are carried out after the pieces are cemented together, in order to have them of the same thickness exactly. If linearly polarized white light falls now upon the double plate from the polarizer, it will exhibit, in consequence of the rotation dispersion in going through the plate, a series of colored bands to each side of the center. The analyzer following will not allow those rays to pass, whose plane of polarization coincides with the principal section of the analyzer. If these are the yellow rays, those remaining which pass through, yield a mixed color of a pale blue violet shade, which, with the slightest turn in the analyzer, turns to either red or blue, and which is designated as the *sensitive or transition tint* (teinte de passage) Inasmuch as the two halves of the biquartz can have the same color only when the principal sections of the polarizer and analyzer are parallel or perpendicular to each other, the two quartz plates are given such a thickness that they rotate the yellow rays to the right and to the left exactly 90° or 180°. For the first, the thickness must be 3.75 mm., since Biot found that 1 millimeter of quartz rotates mean yellow light through 24°, and we have then the proportion, 24° : 1 :. 90° : 3.75. In this case, the principal sections of the polarizer and analyzer must be parallel to secure the transition tint. If the biquartz, on the other hand, is 7.5 mm. thick, so that the yellow rays are rotated through 180°, then the transition tint will appear by crossed position of the Nicols. If the analyzer is now turned a little from its vertical

or parallel position with reference to the polarizer, one-half of the field will appear blue, the other distinctly red. This *simultaneous* appearance of the red and blue colors makes the observation with the Robiquet apparatus more sensitive than where light and shade *follow* each other, as is the case in the Mitscherlich apparatus.

102. **The Observation.**—The Robiquet apparatus requires white light and furnishes us with the angle of rotation for mean yellow light, which, following Biot's suggestion, is represented by α_j. Although the position of the line separating the two halves of the double quartz is a matter of indifference, the latter is generally so placed that the division is vertical The telescope is sharply focused on this line of separation by proper movement of the ocular. The observation tube is not yet to be placed in position. By turning the analyzer it is a simple matter to bring out the transition tint as a perfectly uniform shade on the two halves of the field. The position of the analyzer corresponds then to one zero point of the instrument, the other zero point is separated from this by 180°. If now the tube containing the active liquid is placed in the trough the uniformity of color disappears. The analyzer is then to be turned until the equality of the shades on the two halves of the image returns, the angle through which the analyzer had to be turned is equivalent to the angle of rotation of the substance, α_j. But the latter must not be too large, because it could then happen that the transition tint would no longer be sharply defined. On the relation of angles of rotation, α_j and α_D, see § 152.

In order to recognize whether the active substance is right-rotating or left, it is necessary to determine, once for all, with the particular instrument, the position of the red or blue field when a body with known direction of rotation, right rotating cane-sugar for instance, is between the Nicols. If the substance under investigation shows the same arrangement of the two colors it, likewise, must be right-rotating; if, on the other hand, the shades are reversed, the body must be left rotating. In addition, with a right-rotating body, uniformity of color on the two halves of the field reappears when the analyzer is turned in the clock-hand direction, while with a left-rotating body the motion of the analyzer must be the reverse.

The mean error of a reading is about ± 4 minutes of arc

The apparatus of Robiquet suffers from several drawbacks In the first place it gives a determination of α_j only and can not be used for homogeneous light. Secondly, an absolutely accurate determination of the angle of rotation is not possible, because after putting the observation tube in position, especially if the liquid is somewhat colored, the transition tint never shows exactly the same shade that appeared in the zero point determination, and in consequence of this, indeterminable systematic errors are introduced. Finally, the readings may be quite inaccurate with those deficient in a sharp sense of color, and for the color-blind the use of the apparatus is impossible For these several reasons it is scarcely used at present, and can be employed at most only for approximate determinations of the rotation.

3. Wild's Polaristrobometer [1]

103. **Description of the Instrument.**—This instrument, which was brought out by Wild in 1864, but which to-day finds only limited use, gives much closer results than either of the previously described polariscopes The peculiar feature of the instrument consists in this, that a Savart polariscope is placed between the polarizer and analyzer, the former of which may be rotated, and this combination gives rise to a series of dark bands which disappear with a certain position of the polarizer. This point, which may be sharply observed, is the one looked for in making the readings. For light, the sodium flame is commonly used, but any homogeneous light may be employed

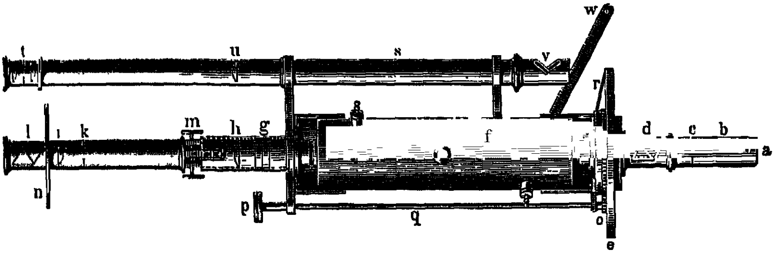

Fig 35

The arrangement of the instrument is shown in Figs 35 and

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[1] Wild: Ueber ein neues Polaristrobometer, Berne, 1865.

36. The identical parts are shown by small letters in Fig. 35 and by large letters in Fig. 36.

A bar of brass, Y, which is supported on a stand, X, and which may be moved either vertically or horizontally, carries at one end the polarizing, and at the other, the analyzing, appliance. Light passes into the tube b through a, and reaches the polarizer d through the round diaphragm c which has a diameter of about 10 mm. The brass work holding these pieces is rigidly attached to the graduated circle e and may be rotated with this, around an axis. The polarized rays pass through the observation tube f and enter then into the fixed ocular part. This, the so-called polariscope, contains first, at g, the arrangement which produces the sensitive interference bands, consisting of two Iceland spar plates 3 mm. in thickness, cemented together. These plates are cut so as to make an angle of 45° with the optical axis and are then laid together in such a manner that their principal sections cross at right angles. Two lenses, h and i, follow, making a telescope of low magnifying power (about 5 diameters), with adjustment for focusing the latter upon distant objects. A round diaphragm, k,

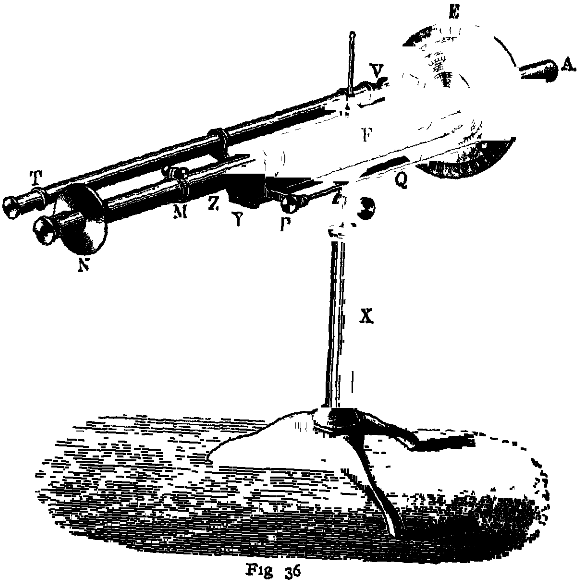

Fig 36

holding cross hairs in X position, and having an opening of about 4 mm., is placed between the two and in the focus of h. Finally comes the analyzer l, which is ordinarily so fastened that its principal section stands horizontally. The crossed principal sections of the double plates g, must make angles of 45° with the latter. In order that the positions of the two parts g and l may remain fixed with reference to each other, the draw-tube of the ocular in which the nicol l and lens i are placed, is furnished with a guide The whole polariscope is contained in a shell Z, attached to the bar Y, and may be rotated through a small angle. For this purpose the shell has a widened guide slit and two set screws, m m, which hold between them a small projecting piece standing out from the polariscope tube. This last arrangement serves for the adjustment of the zero point of the apparatus At n a round disk screen is fastened which keeps outside light away from the eye of the observer.

In order to rotate the polarizer d, the setting holding it, along with the attached circular disk, fits into a solid ring fastened to the bar Y On the side of the disk toward the observer there is a toothed wheel into which the small pinion wheel o works, and this is operated through the rod q by means of the button p Near the periphery of the disk there is a circular graduation, adjoining which is a fixed vernier or simple index r The graduation may be read by aid of the telescope s which consists of the adjustable ocular t and the objective lens u At the end of the telescope, at v, there is a small inclined mirror, with round opening in the center, which serves to reflect light on the scale from a small flame carried on the arm w. Finally, it should be mentioned, the instrument is usually made to hold observation tubes up to 22 cm in length.

104. **The Observation.**—In carrying out an observation, after putting an empty tube in the apparatus to find first the zero point, the polariscope ocular is drawn out until the cross hairs are sharply defined. The polarizer is now turned by aid of the button p (Fig. 35), until a position is found in which the illuminated field appears to contain a number of parallel dark

bands or fringes (Fig. 37, *a*). By continued turning these begin to fade out, and finally a point is reached where a clear part, free from bands, runs through the field. By a slight motion of the button to and fro, this bright part is brought as nearly as possible to the middle of the field leaving, on each side of the cross hairs and equally distant from the center, parts of the fringes still visible. This position is the one at which a reading of the graduation is made. If the polarizer is turned further the bands become stronger to a certain maximum, then weaker followed by disappearance, and in a complete rotation of the circle this phenomenon is repeated four times at intervals of 90°.[1] Ordinarily in each one of these positions the remaining fringes show some characteristic form which should be remembered. The extinction of the bands corresponds to those positions of the polarizer at which its principal section coincides with the principal section of one of the crossed pieces in the Savart double plate, while the greatest intensity of the fringes is found when these sections make an angle of 45° with each other

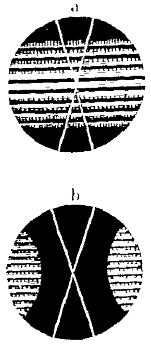

Fig. 37

If it is found that the bright part of the field is so broad that the fringes right and left from the center no longer show, then the luminosity of the source of light must be diminished until the portion free from bands has grown narrow enough. The decrease in the width of the portion free from fringes follows from this, that the eye, on diminishing the total illumination, acquires greater sensitiveness in recognizing differences in intensity, and may therefore follow the fringes further to the points at which they totally disappear, than would be possible with a brighter field.

If the movable Nicol is brought to one of the four zero points, and the empty tube replaced by one filled with an active liquid, the interference bands appear anew. On passing through the active layer, the plane of polarization is rotated through a certain angle, and in order to place this again parallel with one of the principal sections of the Savart double plate, the polarizer must be turned through an equal angle in the opposite direction The disappearance of the bands follows then as before The angle through which the polarizer must be moved to bring about the extinction of the bands is, therefore, the angle of rotation of the body placed between the Nicols. The circular disk must consequently be turned in a direction opposite to the clock-hand motion when the body is right rotating and *vice versa.* In respect to the button P p, Figs. 35 and 36, on which the hand of the observer rests, the motion here corresponds with the direction of rotation of the substance. If the figures on the circle, like those on a clock face, run from left to right, as is usually the case, the readings with a right rotating body give larger numbers and those with a left-rotating body smaller numbers than are shown in finding the zero point In regard to the method of observation and determination of the direction and amount of rotation, see §97 and § 93.

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[1] For the theory of these bands see Wüllner's "Lehrbuch der Physik.," 4th ed , 2, p 650.

The mean error of a reading is about ± three minutes of arc.

β. *Half-Shadow Instruments.*

105. **Principle of the Half-Shadow Apparatus.**—In these polaristrobometers, the characteristic sensitive part is so constructed that the field of view is divided into two or more surfaces, which, with a definite position of the analyzer, show a uniform degree of partial shadow This point is employed in the observation. On account of the relatively low luminosity of the field in the neighborhood of this point, these instruments have received the name of half-shadow apparatus (polarimètres à pénombre).

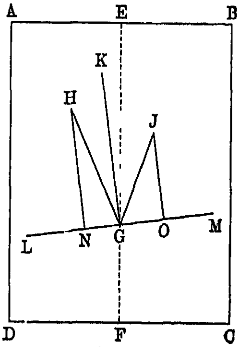

Fig 38

The half-shadow instruments all contain an illumination lens, the polarizing appliance, which does not consist in a simple nicol alone, the analyzer, and a reading telescope. To take the simplest case first, let us consider the polarizer so made that it furnishes a field, A B C D (Fig. 38), which appears to be divided into two halves by the line E F, and in such a manner that all rays coming from the surface A E F D are linearly polarized in the direction of G H, while all rays which come from E B C F are linearly polarized in the direction G J. According to §91, the polarizer will pass always such rays only as are polarized vertically to its principal section. Let now G H $= a$ and G J $= b$ represent also the amplitude of the light vibrations, which, in reality, as will be seen later, never differ much from each other. The angle H G J $= \alpha$, which the two directions of polarization make with each other, is usually made smaller than about 10°. Imagine the analyzer turned so that its principal section G K falls within the angle α, and represent the angle H G K by β Then, when L M is perpendicular to G K, the analyzer allows of a the component G N $= a \sin \beta$ to pass, and of the vibrations b the component G O $= b \sin (\alpha-\beta)$ The smaller the angle α is made, the smaller these two components become; that is, the greater becomes the shadow on the field of view; the angle α is, therefore, briefly termed the *half-shadow* It appears further that for $\beta = 0$, G N $= 0$; that is, when the principal section of the analyzer coincides with the direction of polarization on the surface A E F D, then the surface becomes perfectly dark; likewise, G O $= 0$ for $\beta = \alpha$; that is, the surface E B C F becomes perfectly dark when the analyzer principal section coincides with its direction of polarization The half shadow α may be most simply and easily found when the analyzer is so turned that the one surface is perfectly dark, and then until the other surface is in the same way obscured; the angle between the two positions is equal to the half-shadow α.

As remarked above, in making an observation with a half-shadow instrument, the point for final reading is sought when the two surfaces show exactly the same degree of illumination. This is the case when G N $=$ G O or $\tan \beta = b \sin \alpha / (a + b \cos \alpha)$. From this equation a definite value for β follows; there is, therefore, only one position of the analyzer at which the field shows an absolute uniformity of shadow. Uniform illumination is exhibited also when the analyzer is turned through 180° from this first position, as then the principal section has the same position as before. Accordingly, all half-shadow instruments possess two zero points 180° apart. If the principal section of the analyzer is turned out of the half-shadow angle α and parallel to the junction line of H J, it will follow, too, that in this case the illumination of the two halves of the surface will be the same, but the light is so little weakened by the analyzer that the whole field appears now very bright. But the eye is not able to distinguish slight differences in illumination between two bright lights, and for this reason the position of the principal section parallel to H J cannot be employed in the observations. On the other hand, when the principal section is at its zero position within the small half-shadow angle, the field is pretty dark. The intensities of the light passing the analyzer from the two surfaces are to be taken as proportional to the squares of the two amplitudes, G N and G O, as the vibrations take place simultaneously in the same medium. But these amplitudes, because of the small value of α, are very small as compared with the amplitudes a and b. If then, the analyzer is turned but very little from its zero position, the one surface will become brighter and the other darker, which the eye can sharply recognize, because of the slight general intensity of the whole field. As the polarizing arrangements in all half-shadow instruments are so made that a and b are very nearly the same, it follows from the above equation that in the zero position β is always nearly equal $\frac{\alpha}{2}$ The analyzer principal section is then always so adjusted that it very nearly bisects the half-shadow angle.

As can be seen, the form of the two surfaces, the dividing line between them and their relative positions to each other, do not come at all into consideration One surface may lie wholly within the other, and the line between them be then a circle ; or we can imagine to the right of the surface E B C F another surface which shall have the same properties as the surface A E F D, that is, its light polarized in the direction G H. We have now a field of view in three parts, in which the three surfaces must show the same degree of illumination when again the principal section of the analyzer bisects the half-shadow angle. As will be seen, all these cases have been applied in practice in the most different ways.

106. Influence of the Source of Light.—In all the following considerations, for the sake of simplicity, we shall assume a field of view with double surface, as the explanations hold good, or at most with very slight exceptions, for fields with more divisions. If we illuminate a half-shadow apparatus with homogeneous light of definite wave-length, bring the analyzer to the zero point so that the two fields show the same intensity, and then insert an active substance, the two directions of polarization will be turned through exactly the same angle by the latter. The half-shadow angle α remains, therefore, constant. To find now the amount of rotation of the two planes of polarization, the analyzer is turned until the field of view becomes uniformly shaded as at the start. If now the principal section of the analyzer should not have exactly the same position with reference to the two planes of polarization, which it had when the zero point was found, a systematic error must obtain somewhere and the angle of rotation of the analyzer would not give, directly, the rotation of the two planes of polarization. The principal section will maintain its relative position to the two planes of polarization only when the relation of the intensities of the light in the two fields is not altered by the active substance.[1] But this obtains for homogeneous light as the two intensities are weakened by reflection at the end surfaces and by absorption in exactly the same manner Therefore with homogeneous light the angle of rotation of the analyzer is equal to the angle of rotation of the active substance.

This is the proper place to again emphasize how important it is, and especially with half-shadow instruments, to be certain that the course of the rays through the whole apparatus to the eye of the observer is perfectly correct. If, in illustration, in the above case one of the pencils of rays only were to suffer a partial obstruction by insertion of the active substance, it would necessarily follow that the relation of the two intensities would be altered and consequently a change brought about in the zero point position. It will be recognized also how essential it is that the light which reaches the polarizing mechanism, independently of the distribution of the intensity in the source of light, must be perfectly uniform, as otherwise the relation of the two field intensities would undergo continuous changes. Variations in the total intensity of the light reaching the polarizer would then naturally leave the relation of the intensities of the emerging lights unaltered, and thus give rise to no displacement of the zero point.

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[1] According to §105 $\tan\beta = b \sin\alpha / (a + b \cos\alpha)$, or $\tan\beta = \sin\alpha / \left(\frac{a}{b} + \cos\alpha\right)$; β is therefore dependent only on the relation $a : b$

The question will now be discussed, to what extent the zero point is changed by use of different colored lights in instruments, the polarizing mechanism in which, is unsymmetrically arranged. This is the case, for example, in the Laurent and Lippich polarizers in which the light of one-half of the field has to pass through one more prism than that of the other, from which cause the intensity of the first light is weakened by reflection and absorption. The relation of the light intensities must therefore vary with the wave-lengths, and then the zero point of the apparatus also. As long as one is working with homogeneous light, these zero point displacements amount to but a few seconds of arc, as may be readily found by calculation, but in very exact investigations even this should be considered, as in the best half-shadow instruments the mean error in a reading is counted now by seconds only But the case is very different when white light is used, as is the custom in all half-shadow saccharimeters Then the light on one field is not only weakened, but it becomes changed in composition also, as the absorption and reflections change with the wave-length Zero-point variations up to nine seconds may be found here by employing white lights of different sources. When one considers the difference in the composition of the light on the two fields, it will be understood how the zero point may be altered even a whole minute when at any position between the polarizer and the eye, some substance is placed, for example, a dichromate plate, which absorbs some rays relatively strongly. For this reason, it is therefore wrong in principle in finding small rotations of strongly colored solutions, in order to escape the trouble of procuring an intense sodium light, to examine them in a half-shadow instrument or saccharimeter with white light, and with a degree of accuracy which is but a fraction of the systematic error from zero-point displacement, which may also vary in differently colored substances. This method of finding an angle of rotation with white light will be criticized from another standpoint in § 153.

107. Calculation of the Sensitiveness.—The accuracy which may be reached in half-shadow instruments, is measured by the delicacy with which one can judge of the uniformity of shade on the two surfaces of the field of view. If the analyzer is turned through the small angle $\Delta\beta$ from the position in which the two fields appear to have the same brightness, the illuminations of the two fields may differ by an amount expressed as p per cent. On the assumption that in the zero position, the principal section of the analyzer bisects the half-shadow angle, it may be shown in a very simple manner that between the quantities α, $\Delta\beta$, and p, the relation $p = 400\,\Delta\beta / \tan\frac{\alpha}{2}$ exists, when $\Delta\beta$ is expressed in absolute measure; that is, when $90°$ is taken as $\frac{\pi}{2}$. If $\Delta\beta$ is measured in seconds of arc, then $p = 0.00194\,\Delta\beta'' / \tan\frac{\alpha}{2}$ in per cent.

Let us assume, in order to have an illustration, that the brightness of the field and the sensitiveness of the eye will admit of a photometric accuracy of $p = 2$ per cent., then it follows from the above formula that errors in reading $\Delta\beta$ become smaller in proportion as the half-shadow α is decreased. In the following table are given certain values of α, and the corresponding values of $\Delta\beta$, in seconds, for $p = 2$ per cent.

α	10°	8°	6°	4°	2°	1°	30′
$\Delta\beta$	90″	72″	54″	36″	18″	9″	4″

In order, therefore, to make the smallest error in the reading, the half-shadow must be chosen as small as possible. But inasmuch as with decreasing half-shadow the total illumination at the zero point decreases also, it is not practicable to go below a certain limiting value for the half-shadow, which varies with the intensity of the source of light, because with a field of view which is too dark, the sensitiveness of the eye in recognizing differences in illumination decreases, and p, in consequence, grows larger and with it $\Delta\beta$. For a given source of light the error in reading, $\Delta\beta$, for a certain value of α, reaches a minimum, and the brighter the source of light the smaller may α be to give it. We have then the following rule: *Let the source of light be chosen as bright as possible, and the half-shadow as small as possible, but at least so large that the eye may make the required reading without great effort.*

108. **Methods of Observation.**—We are concerned here with the operations which the observer follows in order to secure equal illumination in the two fields. We shall discuss but a few of the commonly practiced methods which, however, when properly carried out, all yield good results.

If one moves the analyzer rapidly to and fro past the zero point, the dividing line in the field being sharply focused, one has an impression as if made by a band of shadow passing parallel to and across this dividing line over the bright field. Although this phenomenon is purely subjective, since in reality with proper illumination each field is uniformly bright, it is very common in actual practice to stop in the motion of the analyzer at the instant in which this shadow appears to glide over the dividing line However, in this method of observation the analyzer is checked usually a little too soon; this will cause no error only when the mean of a large number of trials is taken, the end point being approached *alternately from one side and the other.* But the hand falls easily into the habit, after turning the analyzer to and fro, of stopping always with the motion from the same side, which naturally introduces a systematic error into the observation.

Another plan very commonly followed is this. The analyzer is turned several times rapidly backward and forward until the differences in shade on the two fields become as nearly as possible the same, and then the fine adjustment screw is turned a little, at random, so as to secure as accurately as may be the mean position between the end positions just reached. This method is naturally applicable only when the fine screw has no lost motion, but gives good results when the contrasts are taken sufficiently small.

A third method of final adjustment is followed by Lippich[1] in all his experiments. The analyzer is turned at first rapidly and then slowly, step by step, and always in the same direction, until apparently uniform illumination is reached; if it is thought that this point is overreached, the analyzer is turned back and the operation repeated. When the point of equal illumination is approached, the eye is opened momentarily only at each step. Of course, one does not reach by this method that position of the analyzer at which objectively the two fields have the same illumination, but a position which differs from this but little, and which depends on the degree of differentiation sensitiveness (about 1 per cent.) in the observer; the analyzer is stopped at that point where the eye is no longer able to recognize a difference in brightness In order to find the real point of equality in illumination, the final adjustment must be made alternately from one side and the other, and the mean of all the readings taken.

It should be made a rule to compare the fields over their whole extent, and after each adjustment to turn the analyzer appreciably away from the zero position because, otherwise, one can fall into the habit of systematically stopping the adjustment at the same wrong point always, and thus unconsciously securing a very small mean adjustment error, which, in reality, may be exceeded several fold by the true error in the result Also avoid, as far as possible, trying to remember with any instrument in which direction the fine adjustment screw must be turned to secure larger or smaller readings on the graduated circle, because in knowing this, the observations may be arbitrarily affected

109. **Jellett's Polariscope.**[2]—In the descriptions of special half-shadow instruments, beginning with this paragraph, only those features of the optical arrangements will be discussed which concern the polarizing mechanism, because the other optical parts are essentially the same in all forms of apparatus. The first half-shadow polariscope was made by Jellett in 1860. Between the polarizing and analyzing nicols, and close to the first, he introduced a prism of the following construction: A

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[1] Lippich. Wiener Sitzungsberichte, II, **91**, 1084 (1885), II, **105**, 323 (1896).

[2] Jellett. Rep Brit Assoc., **29**, 13 (1860)

long Iceland spar rhombohedron, which is converted into a right prism by grinding down its ends, is sawed through lengthwise, making two halves, separated by a plane which makes the small angle $\frac{\alpha}{2}$ with the plane standing perpendicularly to its principal section. These halves are then put together in reversed position, so that the two principal sections no longer coincide but make the angle α, the half-shadow, with each other. This prism is mounted in a tube which carries diaphragms with circular openings at each end, so that the round field of view appears to be divided by the cut into two equal parts The polarizing nicol is so placed that its principal section bisects either the obtuse or acute angle which the two principal sections of the rhombohedron form with each other Light entering the apparatus is first linearly polarized by the polarizing nicol and then passes the spar rhombohedron, in the two halves of which the principal sections are slightly inclined to each other. If the analyzer be now turned so that its principal section is vertical to that of the polarizing nicol, the halves of the field appear uniformly shaded. This is destroyed by inserting an active substance, and in order to secure the uniform shadow, the analyzer must be rotated through a definite angle, which is equal to the angle of rotation of the substance

The Jellett polarizing arrangement was later modified in this way Before cementing together the two sides of an ordinary Nicol prism, one-half is split perpendicularly to the principal section, a wedge, with the small acute angle α, cut out, and then the three pieces united to form a single prism. The cut half, in which the principal sections again form the half-shadow angle α with each other, is turned toward the analyzer in mounting the polarizer in the apparatus. Exactly the same phenomena appear here as in the above case, as indeed the light which passes through the cement layer of the polarizer vibrates still in a single plane only. This Jellett twin prism is often called the Schmidt-Haensch polarizer, because this firm regularly employs it in the construction of their simpler polariscopes.

110. **Cornu's Polarizer.**[1]—This has considerable resemblance to the Jellett polarizer just described, and is made by cutting an ordinary Nicol prism along its whole length, corresponding to the plane of the shortest diagonal, into two halves, then grinding from each surface a small amount, $\frac{\alpha}{2}$, and cementing the pieces together again. This makes a double Nicol prism which has two principal sections, making the half-shadow angle α with each other. From this polarizer the extraordinary rays only can emerge from each side, and we have then a field of view, the two parts of which are so arranged that the direction of polarization of all the rays in the one field makes the small angle α with the polarization direction of the rays in the other field. If the analyzer be then so placed that its principal section bisects this half-shadow angle α, then the field of view will appear faintly, but uniformly, shaded.

The polarizers of Jellett and Cornu have the advantage that any light, compound or homogeneous, may be employed, but they suffer, on the other hand, from the great drawback that the half-shadow angle is a fixed one. In the Laurent polarizer to be now described, it will be seen that the reverse is the case, it possesses a variable half-shadow, but in each single instance may be used for a definite homogeneous light only.

4. Laurent's Half-Shadow Instrument[2]

111. **Description of the Apparatus.**—In the Laurent instrument, illustrated in Fig. 39, the light from a homogeneous source passes through the illumination lens first and then the polarizing mechanism. This consists of the polarizing nicol B, which may be moved by means of a connected lever through a small angle, shown on an arc above, and then firmly clamped, and a thin quartz plate D, which is cut parallel to the optic axis and so cemented to a circular diaphragm that it covers half the opening. At the other end of the apparatus are found the analyzer E and the telescope F. This latter is attached to the circular disk G, and may be rotated with it.

For this purpose a bevel geared wheel is found on the back side of the disk, which works into a small pinion attached to the button H The fixed verniers J, may be read by means of the movable magnifying glasses K

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[1] Cornu Bull. Soc Chim., [2], 14, 140 (1870)

[2] Dingler's poly J, 223, 608 (1877).

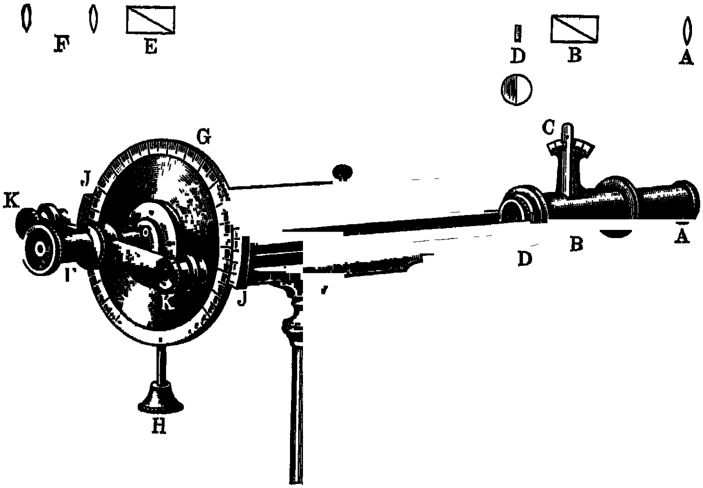

Fig 39

112. Principle of the Laurent Polarizer. — The quartz plate A (Fig 40), covering half of the polarizer diaphragm, must have perfectly parallel sides and must be ground exactly parallel to the optical axis B C The thickness of the plate, d, depends on the wave-length, λ, of the homogeneous light which is employed in illumination This thickness must be so chosen that the two rays, one polarized parallel to the axis of the plate and the other at right angles, which are produced from the light reaching the plate, show on exit a difference in path, δ, which is an odd multiple of half the wave-length. If we represent the ordinary and extraordinary refractive indices of quartz for light of wave-length λ, with n_o and n_e, we have the condition .

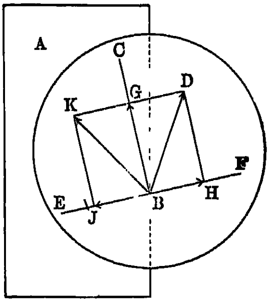

Fig 40.

$$\delta = d\,(n_e - n_o) = (2m + 1)\frac{\lambda}{2},$$

where m is any whole number. From this follows the thickness of the plate,

$$d = (2m + 1)\frac{\lambda}{2} \bigg/ (n_e - n_o).$$

As the apparatus is always constructed for sodium light, λ in this case is 0 0005893 mm , $n_o = 1.5442$, $n_e = 1.5533$, and the minimum thickness ($m = 0$) 0.0324 mm. But as such a plate would be too thin for practical use some odd multiple of this thickness under half a millimeter is taken. Even such quartz plates are usually supplied with a plane glass plate for support If it is desired to make a test to determine whether the quartz plate has the proper thickness or not, the following method may be followed Two Nicol prisms are placed in series in parallel light of the wave-length for which the plate is made, and so that their principal sections are parallel to each other. Between these the quartz plate to be tested is placed and vertically to the rays. If now the plate is turned in its own plane until its optical axis makes an angle of 45° with the principal sections of the prisms, the field becomes dark if the plate has actually such a thickness that it produces a difference in path of an odd multiple of half a wave-length.

Let B D represent the plane of polarization and amplitude of the linearly polarized homogeneous light coming from the polarizer, and let it make the angle C B D $= \frac{\alpha}{2}$ with the optical axis B C The light passing the right half of the polarizer diaphragm is then linearly polarized in the direction B D. In order to avoid unnecessary complication in what follows, it will be assumed that all rays reaching the quartz plate fall upon it perpendicularly, which, in practice, is essentially the case. Then each ray in entering the quartz plate is broken up into an ordinary and an extraordinary ray, whose refractive plane is the principal section ; that is, the plane passing through the axis B C and vertical to the plate. According to §90, this plane is at the same time the plane of polarization of the ordinary ray, while the extraordinary ray is polarized vertically to the principal section. Accordingly, a ray with the amplitude B D on entering the plate is decomposed into the components B G and B H, if E F is perpendicular to B C The ordinary component B G is polarized parallel to the axis of the plate while the extraordinary component is perpendicular to the axis. Both components pass through the plate in a perfectly vertical direction. Now, the thickness of the plate is so taken that the rays polarized parallel to the axis, differ in path by half a wave-length from those polarized perpendicularly to the axis, or in other words, one set suffers a retardation of half a vibration as compared with the other. We can assume that at the moment in which the ray B D reaches the plate, and the decomposition into the components B G and B H takes place, the vibrations of these, in the directions toward G and H, begin simultaneously at B, so that in the moment in which they leave the plate, the one component is half a vibration ahead of the other Imagine further, that in this moment the vibrations begin again at B, and that those of the ordinary component, say, take place as before toward G, then the vibrations of the extraordinary component must be in the direction J, opposite from H. The amplitude B J is, of course, equal to B H, if reflection and absorption are left out of consideration Therefore, two rays polarized perpendicularly to each other leave the plate, whose planes of polarization are the same as within the plate, but which differ from each other in path by half a wave-length At the analyzer, both rays are brought back to the same plane of polarization and, therefore, brought into condition to produce interference But as the difference in path of the two rays is exactly half a wave-length, or an odd multiple of the same, the final result remains unchanged if we replace the two rays B G and B J by the ray B K, whose plane of polarization and amplitude B K, makes the small angle $\frac{\alpha}{2}$ with the optical axis B C The light coming through the plate then is in the condition of linearly polarized light, whose direction of polarization with reference to the principal section of the plate is symmetrical with the direction of polarization of the light coming from the polarizer. Therefore, the field of view is made up of two parts whose polarization directions are symmetrical with reference to the axis of the plate. The half-shadow α is equal to twice the angle which the optical axis of the plate makes with the plane perpendicular to the principal section of the polarizer. If the analyzer is then placed so that its principal section bisects the half-shadow angle, that is, if it is made parallel to the optical axis of the quartz plate, the field will appear uniformly shaded as explained in § 105.

113. **Accuracy of the Laurent Apparatus.**—For the method of conducting the observations, reference is made to §93 and §97, and in regard to the illumination, it may be again remarked that a homogeneous light must be employed in which the Laurent plate produces a path difference of half a wave-length. Instrument makers, up to the present time, have constructed these plates for a sodium light only; the rotations for other rays may not be measured with these apparatus, which is a drawback in their use

The delicacy of the Laurent polarimeter depends, according to §107, on the half-shadow angle chosen. This is variable at will, as the principal section of the movable polarizer may be given any desired position with respect to the axis of the quartz plate But even when a comparatively weak sodium light (Bunsen burner with salt bead) is employed, and therefore a large half-shadow angle of about 8° taken, the mean error of an adjustment amounts to about ± 2 minutes of arc only; with a brighter source of light and smaller angle this may be reduced to below one minute

The instrument maker Heele[1] has lately attempted to increase this delicacy by another arrangement of the field of view. Instead of fastening the Laurent plate in the diaphragm so that it covers one-half of the field, he gives it a circular form and cements it to the center of a larger circular glass plate. The field of view appears then as shown in Fig. 41, concentrically divided.

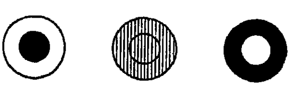

Fig 41

With the Laurent apparatus the angle of rotation may be measured easily within about ± 20″. But if this accuracy is to have a real value the various systematic errors made, depending on the construction of the apparatus, can not amount to more than a few seconds. But the reverse has already been demonstrated by Lippich,[2] in 1890, theoretically as well as practically, who showed that *in general the Laurent apparatus can not be an absolutely exact measuring instrument.* Although Lippich,[1] in 1892, published an abstract of this paper, omitting the mathematical discussion, it seems to have attracted but little notice, since recently several investigators[2] have published very delicate measurements made by aid of the Laurent apparatus. It may be in order then to recapitulate the main results of Lippich's experiments.

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[1] **Heele**. (Berlin O, Grüner Weg, 104) Zeitschr für Instrum, **16**, 269

[2] Lippich Zur Theorie der Halbschattenpolarimeter, Wien Sitzungsber, II, **99**, 695 (1890).

We shall first recall the conditions which must be complied with in order that the light which leaves the Laurent plate may take the form of rays perfectly polarized in one direction only, and see in how far these conditions may be fulfilled. The first condition that all rays reaching the plate must enter it perpendicularly, can never be accurately attained, the phase difference, therefore, produced by the plate is a function of the incident light, from which it follows that this difference for all rays of the same wave-length can not be exactly half a wave-length. The further conditions that the plate must be perfectly plane parallel, that it must be ground exactly parallel to the optical axis, and that, above all else, it must have exactly the right thickness, are requirements which can never be found satisfied in the same plate Besides this, it must be considered as a piece of good fortune to find a perfectly homogeneous quartz plate In spite of all these errors it is true that all the ordinary and extraordinary component rays leaving the plate are linearly polarized, but the planes of polarization of all the ordinary rays taken by themselves, and the planes of polarization of the extraordinary rays considered among themselves, no longer coincide, and the path differences may then vary from each other appreciably. *In other words the light emerging from the plate may exhibit all forms of elliptically polarized rays.* The whole series of rays are then brought back by the analyzer to the same plane of polarization where they interfere. If it is further recalled that the Laurent instrument is always constructed for sodium light, which is by no means perfectly homogeneous light, the possibility must be admitted that because of the consequent variations in path difference the final effect of interference must differ from one apparatus to another, and that the light leaving the analyzer of one apparatus must have a composition different from that leaving the analyzer of another. If the rotation dispersion of the active substance, whose angle of rotation is being measured, is also considered, it will follow, without anything further, that the observed angle of rotation may differ in different instruments. It remains to show that these differences may be quite appreciable

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[1] Lippich Ueber die Vergleichbarkeit polarimetrischer Messungen, Ztschr fur Instrum., **12**, 333 (1892).

[2] Rodger and Watson: Phil. Trans. London, **186 A**, 621 (1895), Ztschr phys Chem., **19**, 323 (1896).

As we shall see later, *the light in the Lippich half-shadow instrument remains always linear and polarized in the same direction*, so that in these instruments no differences should be found in measuring one and the same rotation. Now let the same constant angle of rotation be found in a Lippich apparatus, then in several Laurent instruments, one after the other, the same constant sodium flame being used in all cases. Then the readings of the several Laurent instruments will show variable results compared with that of Lippich. In the theoretical part of his paper Lippich shows this The difference between the angles of rotation measured by a Lippich and Laurent instrument is proportional to the size of the angle, and the proportional factor is a function of the half-shadow of the Laurent apparatus and the construction of the Laurent plate. Therefore, in one and the same Laurent instrument, the observed angle of rotation will vary with the half-shadow. When definite numerical values, such as are found in practice, are substituted in his equations, differences amounting to ± 160″ result in measuring an angle of rotation of about 22°. It must be further considered that Lippich, in his calculations, assumed all the above conditions fulfilled, and deals here with this case alone that the Laurent plate can have the right thickness only for a definite wave-length of the sodium light. In reality, therefore, still greater differences might appear

Experiments made by Lippich are in accord with his theoretical considerations. A quartz plate used had a constant angle of rotation of about 24°. The sodium light used was filtered through a dichromate solution and a copper chloride solution of known strength, so that color differences left were extremely minute. From a number of measurements agreeing well among themselves, it was found that the differences between the readings of a Lippich instrument and two Laurent instruments amounted to 45″ and 82″. *The indications of different Laurent polarimeters, and of one and the same instrument with different degrees of shadow, can vary among themselves and with the Lippich apparatus by amounts which are greatly in excess of the possible and admissible errors of observation.* The conclusion is warranted that an angle of rotation measured by a Laurent half-shadow polarimeter cannot be depended upon as correct within 0.2 per cent

5. Lippich's Half-Shadow Polarimeter.[1]

114. **Instrument with Double Field.**—The polarizing mechanism of Lippich combines variability of the half-shadow with use of any heterogeneous or homogeneous light, and thus satisfies the two requirements which should be met in the most perfectly constructed half-shadow instruments The construction of the Lippich polarizer is extremely simple In front of the polarizing nicol A (Fig. 42), there is a second small nicol B, which is turned toward the analyzer and covers half the large one; it is, therefore, designated as the half prism. It is so adjusted that the sharp edge C, shown as a point in the figure, lies in the axial plane of the apparatus and divides the round polarizer diaphragm D into two halves. The tele-

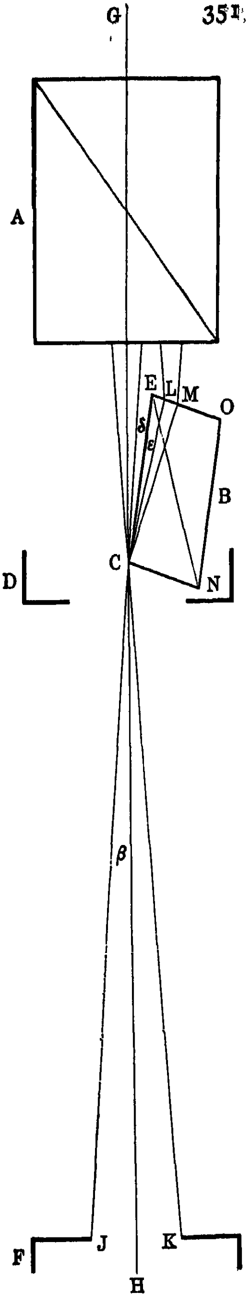

Fig 42

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[1] Lippich · Naturwissenschaftl. Jahrbuch "Lotos," new series, II, 1880; Ztschr. für Instrum 2, 167, Wien Sitzungsber, II, 91, 1081; Ztschr. für Instrum, 14, 326; Wien. Sitzungsber. II, 105, 317

scope focuses on the edge C. While the half prism is fixed, the large prism A, in order to change the half-shadow, is made movable around the axis of the tube. The principal sections of the two prisms may make with each other the small angle α. Then the light coming from A and passing through the free half of the field of view is polarized vertically to the principal section of the prism A. The other part of the light from the same prism is decomposed into two components on entering B, and of these, only the rays vertical to the principal section of the half-prism are able to pass through. The light, then, which comes through the covered half of the field of view is polarized vertically to the principal section of the half-prism. We have, in consequence, a field made up of two halves whose directions of polarization make the small angle α with each other *At the same time, the light of each half remains linear for all wave-lengths, and polarized in the same direction, so that the Lippich polarizer must be considered as the most perfect of all half-shadow constructions.* As a part of the light reaching the half prism is reflected, absorbed, and extinguished in passage, the intensity of the covered half of the field is always smaller than that of the free half. In the zero-position, therefore, the principal section of the analyzer cannot exactly bisect the half-shadow angle, but must make with the polarization direction of the whole prism a smaller angle than with the polarization direction of the half-prism. Consult §105 to §108.

The half prism requires a special construction and adjustment. It cannot be made simply by mounting a prism with right end surfaces so that one side surface C E falls along the axis of the apparatus, because in that case the cone of rays passing in the neighborhood of C E would be partly cut off If F is the circular analyzer diaphragm, and if a perfectly normal passage of the rays is provided for, according to §96, then each half of the field of view will possess uniform brightness in case each cone of rays from any point of the field of view, whose base is the analyzer diaphragm F, if followed back to the prism A, is found to undergo no partial obstruction by the half-prism, and all the ray cones which belong to points on the free side of the edge C, when prolonged backwards do not fall in part through the half-prism, and all other ray-cones which belong to points on the covered side traverse the half-prism completely. These conditions may be perfectly fulfilled. Let G H be the axis of the instrument. We shall consider first a point in the field on the free side, and very close to C. Call the angle J C H, half of the cone J C K, β, which is determined by the analyzer diaphragm and the distance of the latter from the polarizer diaphragm, since $\sin \beta = J K / 2 C J$. If now, the side surface C E of the half-prism is given an inclination to the axial plane, which is a little larger than β by the amount δ, then the cone of light J C K, when prolonged backwards, will reach the prism A without suffering a partial obstruction by the half-prism. This naturally holds true for all the cones of light which belong on the free side and farther away from C. If the surface C E of the half-prism is polished, it is clear that all rays reaching it on the outside from A will be reflected to one side so that they cannot pass through the analyzer diaphragm J K. Consider next the cones of light corresponding to the side of the field covered by the half-prism, and J C K is now the cone belonging to a point on this covered side, infinitely near to C. Followed backwards this, of course, passes into the half-prism and will pass through it without being partially cut off, in case the prism is so constructed that the ray K C is bent in the direction C L, because then J C, still further within the prism, will be refracted, say to M. The half-prism must be so constructed that the ray C L makes still a very small angle ε with the surface C E. In order to secure this, the half-prism cannot have perfectly perpendicular end surfaces, but the angle E C N $= \gamma$ must be somewhat larger than 90°. A simple calculation gives the value $\gamma = 90° + 4\beta + 3\varepsilon + 2\delta$, when ε and δ are made about 10′. According to the dimensions of the apparatus, γ must be, therefore, between 92° and 94° But care must be taken to have the optic axis of the half-prism stand vertical to the long edge C E, and at the same time parallel with or, better, vertical to the refractive edges E and N. Now as regards bundles of rays from points further away than C, it is seen that they all make smaller angles with the perpendicular to the surface C N than does the ray K C, from which it follows that all these rays pass the half-prism without obstruction. But all other rays which pass within the angle ε, or fall on the inner polished surface of C E, are so thrown to one side that they cannot reach the analyzer. A small portion of the surface E O, in the neighborhood of the edge E; that is, the part E L remains, therefore, quite inactive, so that any lacking sharpness of this edge is of no importance *But the edge C must be perfectly sharp and free from faults. In this way, the two halves of the field possess perfectly uniform illumination up to the dividing line, and if the edge C is made with a proper degree of accuracy, at the end of the zero-point adjustment it will be scarcely visible; this is a requirement for an easy and accurate reading.*

Unfortunately, the opticians do not always adjust the half-prism in the manner just described, so that in the zero-point reading, the edge C appears as a thick black dividing line between the two fields, which interferes very materially with the accuracy of the observation But this fault may be in part, at least, corrected by giving the diaphragm placed immediately in front of the source of light a rectangular form, its longer sides standing perpendicular to C, and about four times as large as would appear necessary from the dimensions of the illuminating lens and analyzer diaphragm. In this manner a very fine dividing line is secured again, but toward the end of the adjustment a narrow, somewhat brighter, space appears parallel to C between the two fields which, however, is by no means as annoying as the sharp black dividing line. It must be again said that in a properly constructed Lippich polarizer, the dividing line made by the edge C may be caused to disappear completely in the final reading.

In regard to the accuracy of the Lippich apparatus, it may be remarked that with a sufficiently bright light, and a half-shadow angle of one degree, the mean error of a reading is about ± 15 seconds of arc; but the adjustment must be made from both sides and the error taken as the variation from the mean of all the determinations.

115. **Instruments with Triple Field.**—A field of this kind may be secured by placing two half-prisms B and C in front of the large polarizing nicol A, in symmetrical position, as shown diagrammatically in Fig 43. The sharp edges E and F, which are

brought into focus by the reading telescope, divide the circular field made by the polarizer diaphragm D into three fields, H, J, and K. The width of the middle field J must not be made too large, in order that the two dividing lines may be easily seen at the same time. With a field of view not too large, the middle field is chosen so as to have the areas of the three fields about equal. What was said in the last paragraph about the construction and adjustment of the half-prism holds strictly here also.

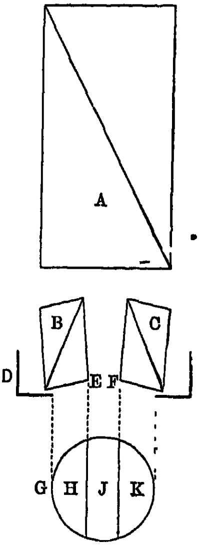

Fig 43

If the principal sections of the two half-prisms are accurately parallel, and if they make the half-shadow angle α with the principal section of the Nicol A, which is movable around its axis, then when the analyzer is turned so that the two fields H and J have the same brightness, the field K must be equally bright, in case the two half-prisms are of the same construction. But above everything else, it is important that the two side prisms should have the same extinguishing power ; this may be most readily tested by employing an intense light and turning the analyzer to the position of greatest darkness with reference to the side fields The prism A is then turned to make the middle field as dark as possible ; in this situation, any inequality in the side prisms may be most readily recognized

The advantage in this arrangement in which equal illumination is secured in three fields over that with two fields, consists in this increase in the fields in which comparison of brightness may be made, and is favorable as long as the dimensions of the individual fields are not too small.

This fact should be especially mentioned that the principal sections of the two side prisms need not be exactly parallel with each other; indeed the following considerations will show that a little distortion of the position of one with reference to the other increases the sensitiveness of the readings. First let us imagine the half prisms exactly parallel, and the analyzer in that position in which the three fields, objectively considered, have the same brightness, then it will be necessary to turn the analyzer to the right and left through a certain small angle β, dependent on the half-shadow angle α, in order to just see a distinction between the middle fields and the side fields. 2β is then the measure of the uncertainty of adjustment with this arrangement; of course, leaving the increase of fields out of consideration, the interval of uncertainty with the double field may be taken as 2β also But if we turn one of the half-prisms by the amount of the angle β from its parallel position, by which the half-shadow angle α for the turned prism is not sensibly changed, because of the smallness of β (see §107), then the conditions become different. In the neighborhood of the zero position of the analyzer, in which all three fields have nearly the same brightness, a difference between the side fields H and K will be always just noticeable. If now we give the analyzer such a position that objectively, for example, the middle field J has the same brightness as H, and in which, in consequence, a difference between J and K is just distinguishable, then the rotation of the analyzer through the angle β, in a certain direction, is sufficient to make a difference between J and H just apparent. The interval of uncertainty in the adjustment is now β; that is, just half as great as before. If we take as the limiting value for this uncertainty in delicacy $p = 1$ per cent., the angle β which the principal sections of the two side prisms must make with each other in order to secure the maximum of delicacy is given, according to §107, by the formula, $\beta = 515 \tan \frac{\alpha}{2}$, in seconds of arc. The polarizer must be, therefore, so constructed, that all necessary movements of the prisms may be made after they are placed in the apparatus. Inasmuch as double the accuracy may be secured with the triple field as is possible with the double field, as indeed Lippich has shown by observations, the polarizer with triple field has already come into general use.

116. Instrument According to Lummer with Quadruple Field.[1]— In this, it is not the uniform brightness of different fields, *but*

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[1] Lummer Ztschr für Instrum, 16, 209 (1896)

the equally strong appearance of two fields on a uniform background which is taken for comparison. With this arrangement the fields are so polarized that on turning the analyzer in one direction from the zero-position, the one field of contrast becomes brighter in comparison with its background, in proportion as the other becomes darker. In order to secure these relations, four polarization prisms must be used, so that four fields result. In front of the large polarizing nicol A, as shown in Fig. 44, there is, first, the moderately large half-prism B, and then in front of this, the two smaller half-prisms C and D in symmetrical adjustment The field of view F, bounded by the round polarizer diaphragm opening E, appears then divided by the sharp edges of the half prisms into the four fields G, H, J, and K After the prisms A and B are given such a position that their principal sections make the half-shadow angle α with each other, the analyzer is turned until the two fields H and J have the same illumination Then the two half-prisms C and D are adjusted with their principal sections turned so that the fields G and K differ to the same extent in brightness from the two middle fields; that is, until these side fields are either lighter or darker than the middle fields, and in the same degree The accuracy of the adjustment is greatest when the contrast is chosen as about 4 per cent On now turning the analyzer from its zero position, that change follows which is peculiar to the contrast principle; while the two middle fields become unequally bright, the contrast between the fields G and H is diminished in the same degree in which that between J and K is increased, or *vice versa*. As, however, the telescope cannot be focused on the three edges, sharply, at the same time it is best not to depend on the help which a comparison of the two middle fields would afford, but to focus on the sharp edges of the two side prisms

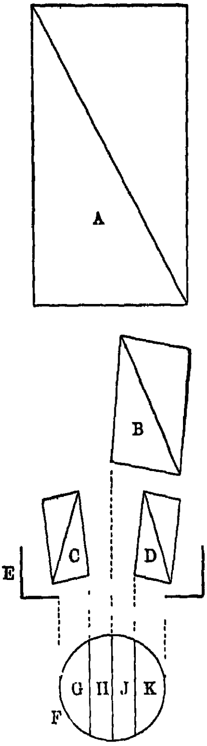

Fig 44

C and D. Any lack of sharpness in the middle line is then of no importance, as in the neighborhood of the zero position of the analyzer, the two middle fields have the same brightness. But up to the present time fuller results as to the practical working of this somewhat complicated contrast polarizer are lacking.

6. *Mechanical Constructions of the Lippich Polarization Apparatus*

117. Landolt's Apparatus.[1]—In order to avoid repetitions, it may be recalled that the part of the apparatus turned toward the source of light contains, always, the illumination lens and the Lippich polarizer with double or triple field, while at the other end of the instrument are found the analyzer, the telescope, and the graduated circle. Landolt has given the Lippich apparatus a form, making it suitable for use in chemical laboratories, so that not only may tubes be examined in it, but vessels of any shape may be inserted between polarizer and analyzer. This instrument is illustrated in Fig. 45 and consists of a strong iron bar, a, on one end of which are attached the analyzer, turned by the lever c, the graduated circle b, and reading microscopes (for reading to 0.01°), while at the

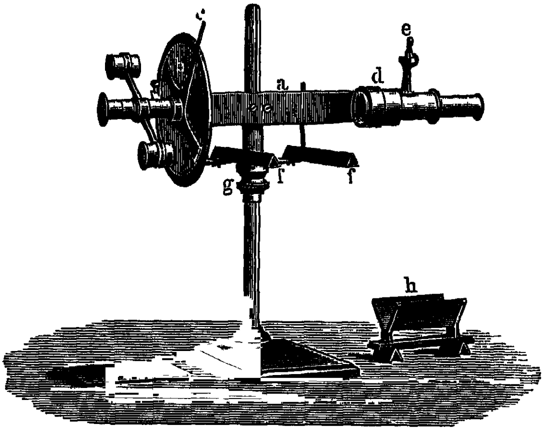

Fig 45

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[1] Landolt "Ueber eine veranderte Form des Polarisationsapparates fur chemische Zwecke" Ber d chem. Ges., 28, 3102 The instruments are made by Schmidt and Haensch, Berlin

other end there is the polarizer d, whose movable prism may be adjusted to change the half-shadow angle by means of the lever e. The whole combination may be attached to a strong Bunsen stand and clamped fast. The guide sleeve is furnished with a thread below, and the nut g, by which means a horizontal arm holding at its ends two prismatic carriers f f may be moved up or down. Two small steel rods dropped from the bar a provide for perfectly vertical motion. The trough h which is intended to hold polarization tubes may be attached to the carriers f f and moved up or down until the tube is brought into the axis of the apparatus ; the final vertical adjustment is accomplished by aid of the screw at g ; the trough h is also slightly movable on its bed plate, through a small angle. Besides this, a brass plate i may be placed on the carriers instead of the trough, and this serves to carry vessels of glass. For the investigation of substances in strongly heated or molten condition, or for the application of very low temperatures, the arrangement in Fig. 46 may be used This is a rectangular brass box, through which a gold plated brass tube passes, the projecting ends of which may be closed by glass plates and screw caps A narrow tube which is soldered to this observation tube, and which passes through the movable top of the box provides for the expansion or contraction of the active substance filled into it. Besides this there are openings in the cover for a thermometer and stirrer. If the box is filled with some substance suitable for a bath, and heated by means of a lamp placed beneath, it is possible to study the rotating power of bodies at any desired high temperature ; it is advisable to cover the box with a protecting layer of asbestos and put up screens to protect other parts of the apparatus as far as possible from the high temperature. If the box is filled with a freezing mixture for investigations at a low temperature, it is necessary to attach glass cylinders, furnished at the ends with plane

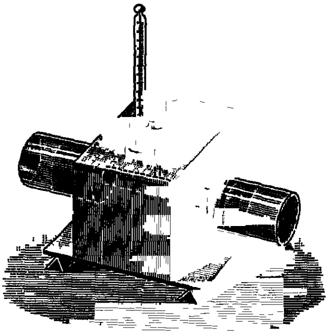

Fig 46

glass plates, to the screw caps and put in these a little calcium chloride to prevent precipitation of moisture.

118. **Apparatus with Adjustable Length.**[1]—In many investigations it is an advantage to be able to change the distance between polarizer and analyzer at will. Fig. 47 illustrates the construction of apparatus in which this is possible, the supporting parts being made intentionally heavy. In this the carriers of the optical parts A, B and C may be moved along a strong cast-iron optical bench D and clamped fast by the screws E in any desired position. Then motion in a vertical direction is made possible by the rack and pinion mechanism at F and the set screws G. C supports a glass trough made to

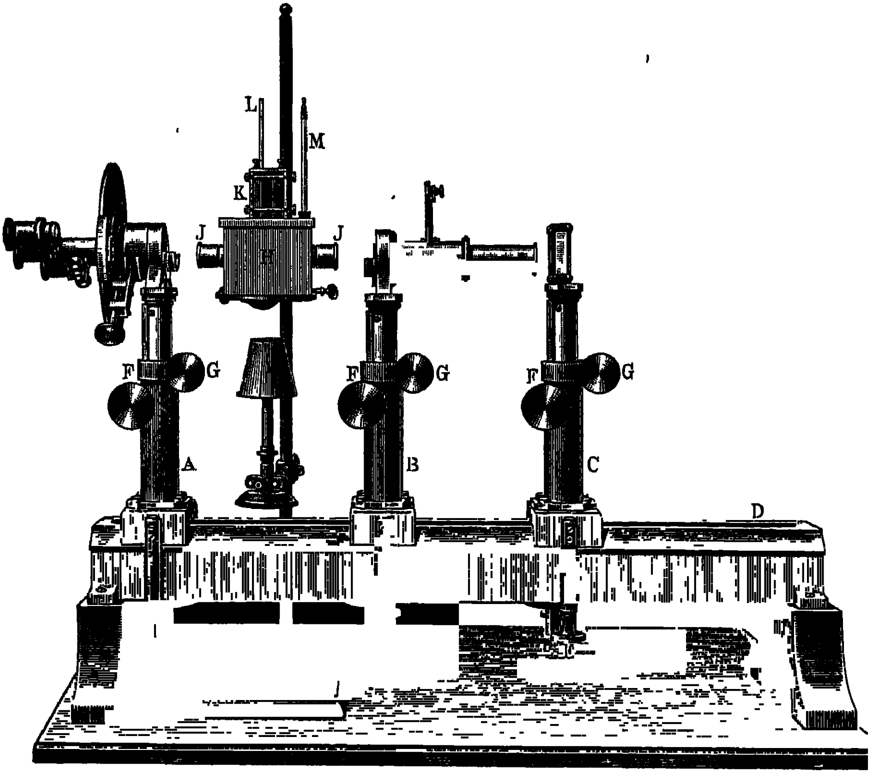

Fig 47

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[1] From Schmidt and Haensch, Berlin

contain solutions for the purification of the light, B the illuminating lens, and the Lippich polarizer, A the analyzer, the telescope, and the graduated circle. Here, also, any desired vessels may be inserted between the polarizer and analyzer. In the figure, a heating vessel and air-bath are shown, which, in some points, are different from the construction described in the last paragraph. The box H, of brass, serves as an air-bath, and has at the sides two projecting tubes J with glass caps. The cell to hold the substance to be investigated, K, is shown in the figure on top of the air-bath H. At the time of experiment, this is brought down into H, and in central adjustment on a little table at the bottom of H. The cell K is made of brass and nickel plated; but the two ends through which the polarized light must pass are made of parallel glass plates. The screw cover of the cell, and corresponding to this the cover of the air-bath H contains two holes through one of which in each case the little tube L passes, which permits the expansion of the substance during warming, while through the other openings, the thermometer M may be introduced into the cell K.

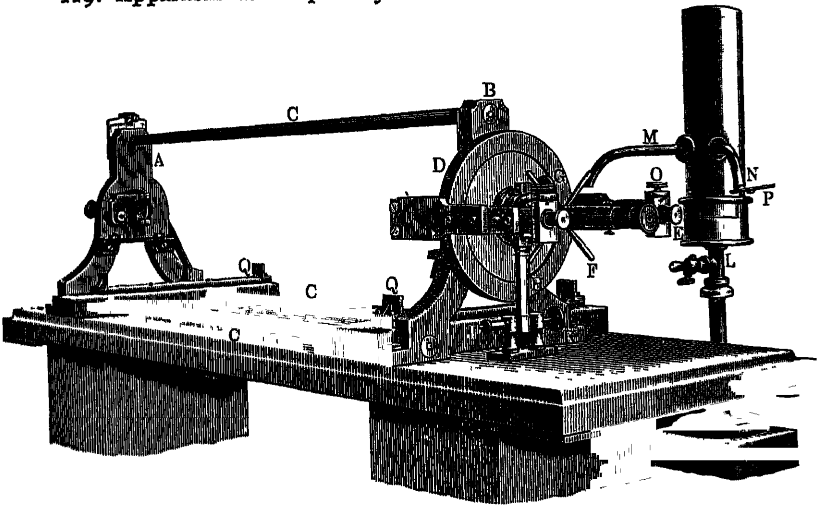

Fig 48

119. **Apparatus for Especially Exact Measurements.**[1]— The large apparatus shown in Fig. 48 permits a very accurate reading

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[1] From Schmidt and Haensch, Berlin

of the graduated circle. Two strong cast iron carriers, A and B, each of which ends in two legs, are attached in vertical position by aid of three horizontal, nickel plated brass rods C, and with these constitute a heavy solid stand. This is screwed down to a thick wooden base through the four legs, of the two carriers one, A, serves to hold the illuminating lens and the Lippich polarizer, the other, B, supports the analyzer, the graduated circle, and the telescope. For protection of the graduation, the circle is covered with the case D, which has two mica covered openings in the neighborhood of the two reading telescopes E. By aid of the four arms F, the graduated circle may be rotated on its axis, it may be fastened by the clamp screw G, and then the more delicate motion may be accomplished by aid of the lever H, the lower end of which rests against a point attached to a spiral spring J on one side, and on the other, against the micrometer screw K. With this construction, it is possible to move the circle and the attached analyzer rapidly to and fro across the zero position without any lost motion, which is very advantageous for the observation. The illumination of the circle is provided for by the two gas-lamps L (only one is shown in the figure), the light from which is reflected on the circle by aid of the bent glass rods M which are blackened on the outside, while at the same time the movable glass arm N illuminates the notebook of the observer, and one of the two micrometer screw-heads O. The light from N may be shut off by turning the black screen P The illumination may be still more easily accomplished by aid of small incandescent lamps attached in the right positions On looking through one of the reading telescopes E in making the observation, an image such as is illustrated in Fig 49 is seen The two parallel threads running through the field between the marks 198 and 199 serve as an index These threads may be moved in a vertical direction by aid of the screw-head O. To count the revolutions, the micrometer is furnished with a counting scale in focus of the ocular; the motion from tooth to tooth corresponds to a complete revolution of

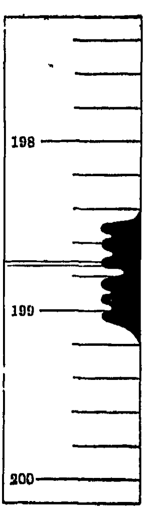

Fig 49

the head. One point on the scale is distinguished by a deeper indentation, and from this the rotations of the screw-head made are counted. One full revolution of the screw-head corresponds to half the interval between the two division marks on the graduated circle, that is to 0.1° Now, as the head is divided into 50 parts, one of these must equal 0.002 The threads are to be so adjusted that they pass through the deep indentation of the counting scale when the index of the screw-head is at the zero point on the screw-head graduation This is the fixed zero position of the threads from which the observed rotation is estimated; in the figure the threads are shown a little away from this zero position. The reading, in the case illustrated by the figure, would be made in this way. 198.7° is first read. Then by turning the screw, the threads are brought into such a position that they include the division 198.6° centered between them In the illustration it will be necessary to give the screw-head over one complete revolution to accomplish this. If the figures on the head graduation run so that larger numbers are passed in doing this and, if finally, the index stands at 36.5, then 36.5 × 0.002° must be added to the first reading of 198.7°; that is, the complete reading is 198.773° In these instruments, the large circle is usually divided into 400°, from which it follows that the figures so read off, must be multiplied by 0.9 to obtain the true degrees of arc.[1] As it is not difficult to read 0.0009° in this manner, and as the mean error of reading an adjustment is about ± 0.0005°, it must be determined whether or not the errors due to lost motion along with periodic and continuous errors in the screw are all below 0.0005°, if one is to be certain of introducing no systematic errors in the final result Two complete micrometer screw-head revolutions must correspond with the same degree of accuracy to the interval between any two divisions on the graduated circle. That such an accurate reading is not illusory, will be admitted when it is remembered that under favorable conditions the mean error of an adjustment is less than ± 0.002°.

The apparatus shown in Fig. 48 is suitable also for the investigation of electro-magnetic rotations. The spools to hold the copper wire coils and observation tubes are carried on sliders which work on the two brass rails Q, so that they may be easily shunted in or out of the field as desired.

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[1] As no great amount of work is required for this multiplication, it must be considered as inexcusable in scientific publications to report figures for a periphery of 400°, because in this way, lasting errors will be introduced into the literature.

120. Allowance for the Earth's Magnetism.—As the large apparatus just described may be used in very exact determinations, this is the proper place to add a few remarks on the extent of the influence of the earth's magnetism in the measurement of an angle of rotation. The amount of the electro-magnetic rotation of the plane of polarization depends on the substance, and is proportional to the length of layer and to the intensity of the electric or magnetic field component parallel to the direction of the light rays. Most substances possess a positive magnetic rotating power, that is, they turn the plane of polarization in the same direction in which the galvanic current which may be considered as producing the magnetic field flows. Therefore, in considering the influence of the earth's magnetism, as the light rays always pass horizontally through the apparatus, we are concerned only with the horizontal component of the earth's magnetism,

$$H = 0.19 \left[cm^{-\frac{1}{2}} g^{\frac{1}{2}} s^{-1} \right].$$

If then the effect of the earth's magnetism is to be wholly avoided, the axis of the apparatus should be placed perpendicularly to the magnetic meridian. If the axis lies in this meridian, the effect of the earth's magnetism on the rotation, φ, reaches a maximum. If, besides this, the light rays pass in the meridian from north to south, the rotation of the plane of polarization is in the negative direction. In order to give an idea of the maximum value of the magnetic rotation, φ, the following figures for sodium light are sufficient: for a quartz plate, 1 mm. thick, ground perpendicularly to the axis $\varphi = 0.021''$. In quartz investigations, therefore, the influence of the earth's magnetism is of no moment. But the case is different with tubes of liquids. If the tube contains pure water, this and the end plates also rotate the plane of polarization. While the effect of the latter is always very small, since for a plate of glass 1 mm. in thickness, φ is $0.049''$, the rotation of a column of water, 20 cm. in length, is $\varphi = 3.0''$;

that is an amount which must be taken into consideration in exact investigations, certainly at least in the calculation of errors. It is always best to place the axis of the apparatus perpendicular to the magnetic meridian so as to wholly eliminate the magnetic effect It may be remarked in conclusion, that the magnetic rotation in gases and vapors may be wholly neglected

7 *Lummer's Half-Shadow Apparatus*[1]

121. Description and Theory of the Instrument.—As it has not yet been fully described, the illustration in Fig 50 is only diagrammatic, and the discussion will be brief The hypothenuse surface A B, of a right angled glass prism A B C, as free as possible from any strain, is silvered and a part of the silver layer removed Care is taken to have the two fields join each other with perfectly sharp edges, and that they have a position perpendicular to the refractive edge of the prism. The illuminating lens D is placed in front of one of the side surfaces of the prism A C, and between them the polarizing Nicol E, so that the light rays suffer total reflection on the hypothenuse surface A B The analyzer F and the telescope G H J face the other cathetus surface B C, and the two hypothenuse fields are brought into focus Imagine the polarizer placed at first so that its principal section is vertical to the plane of reflection; that is, so that the plane of polarization forms zero angle with the plane of reflection, then the light reflected from the glass and silver surfaces, and passing through B C is rectilinearly polarized and in the plane of reflection. The two fields appear uniformly light or dark with any position of the analyzer F. But if the plane of polarization of the polarizer E be turned through the angle $\frac{\alpha}{2}$ away from the position parallel to

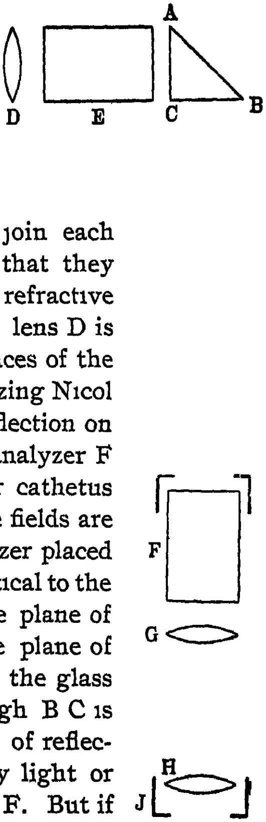

Fig 50.

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[1] Lummer Ztschr. fur Instrum 15, 293 (1895)

the plane of reflection, then the planes of polarization of the light reflected from the glass and silver surfaces, are symmetrical to the plane of reflection and the two fields behave as half-shadow fields, whose half-shadow is equal to α. Of course, a division into three or any number of parts may be made in the simplest manner in the field of view. But it is difficult to secure a glass prism perfectly free from distortion strains, and to prevent such from appearing during an observation. There are noticed, therefore, even with small half-shadows, brighter or darker parts in the field of view. Further, the light leaving the prism is not absolutely linearly polarized, but also elliptically, and this the more strongly, the larger the half-shadow. For the reasons mentioned in §113, the apparatus should not, therefore, be used in exact measurements.

b. Saccharimeters

122. Simple Wedge-Compensation.—The saccharimeters largely used in practice, serve especially for the determination of the strength of sugar solutions Such a determination may be made with any of the instruments described above, but they require homogeneous light; to be able to use ordinary white light in practical work was the leading factor which led to the construction of the saccharimeters. This problem was solved in 1848 by the *wedge-compensation* of Soleil, which is the *characteristic part in all saccharimeters.* This will, therefore, be described first, but it may be remarked that a full discussion of the theory of wedge-compensation would lead too far here, and it must be left for a special treatment.

As already explained, quartz plates cut perpendicularly to the axis rotate the plane of polarized light, and rather strongly, since a plate 1 mm. in thickness turns the plane of sodium light about ± 21.72°. In order to simplify the following considerations we shall assume any of the polarization instruments as illuminated by homogeneous light. We place the analyzer in the zero position, or as we may briefly express it with Fric, in the position of *optical equilibrium.* Then bring between the polarizer and analyzer any positively or negatively rotating substance and the optical equilibrium will be destroyed, which may be restored again, without turning the analyzer by adding, also between polarizer and analyzer, a negative or positive quartz plate of such thickness that the algebraic sum of the rotations of the active body and the quartz is equal to zero. It is then said that the *rotation of the body is compensated by the opposite rotation of the quartz*. The Soleil wedge-compensation is nothing but such a quartz plate, whose thickness, within certain limits, may be changed so as to compensate any desired rotation within limits Of two equally thick, plane parallel quartz plates, cut perpendicularly to the axis, the negative one A B C D and the positive one E F G H, Fig 51, imagine one, say the latter, divided by a cut, vertical to the plane of the paper, into the two wedges, E J K H and J F G K, and that the last is enlarged to form the wedge L M N. The large and the small wedge have now the same wedge-angle. The whole wedge-compensation is situated between the polarizer and analyzer, so that the light rays pass in and out from the surfaces B C and E H, the negative plate and the small wedge are fixed, while the large wedge may be moved along J K In moving the long wedge, the surfaces E H and M N remain always parallel, so that the two wedges form a positive quartz-plate of variable thickness. In the position of the plates illustrated in the figure, the whole compensation gives the rotation zero, as E F = A B If the long wedge is moved so that L approaches J, the thickness of the positive plate will exceed that of the negative, and the wedge-compensation will produce a positive rotation with which the negative rotation of an active body may be compensated. If, on the other hand, the large wedge is shoved in the opposite direction, so that N approaches K, then the thickness of the negative plate is in excess, and positive rotations which are not too large may be compensated. The greatest possible change in thickness is secured, the longer the large wedge is

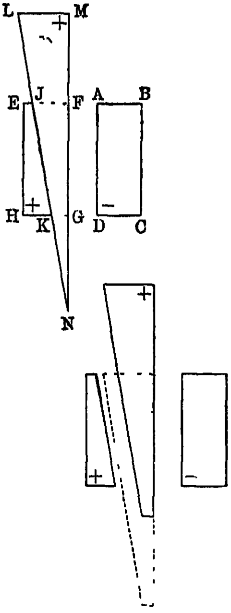

Fig 51

made, and the greater the wedge angle. Practically the long wedge is not shoved along J K, but the two wedges are separated as shown in Fig. 51 below, and then the long wedge is so moved that the surface M N remains in the same relative position parallel to E H. But as the layer of air remaining between the two wedges effects a lateral displacement of the whole system of rays going through the apparatus, the two wedges are separated no further than is absolutely necessary to permit the free motion of the large wedge. This displacement of the rays by the air explains also why the wedge-compensation does not give exactly zero rotation when the thickness of the two wedges together is exactly equal to that of the negative plate. If the mounting of the large wedge is furnished with a scale, the displacement of this, with reference to a fixed vernier, is directly proportional to the change of thickness of the positive plate.

Now, let us suppose the apparatus illuminated by white light, it being assumed, of course, that the polarizer permits this, which is the case with the accurate Lippich half-shadow instrument, and let the analyzer be turned to optical equilibrium Then on inserting the wedge-compensation again between polarizer and analyzer, it will be found that optical equilibrium is restored when the large wedge is turned so as to indicate zero rotation. This appears simultaneously for rays of all wave-lengths, because the rotation dispersion is the same for positive and negative quartz-plates *But, at the same time, it is found that because of this rotation dispersion, the rotation of such active bodies only, as have the same dispersion as quartz, may be compensated by the wedge-combination.* The rotation of quartz-plates in the first place may be compensated, and also that of sugar solutions, since, as shown in §45, the rotation of cane-sugar is very nearly the same as that of quartz. It is because of this fact that the construction of saccharimeters, which may be employed with white light, is possible.

123. Double Wedge-Compensation of Schmidt and Haensch — In the double wedge-compensation system introduced in saccharimetry by Schmidt and Haensch, the negative plate of Fig. 51 is replaced by two negative quartz-wedges of the same angle, so that the negative as well as the positive plate possesses a variable thickness. This double wedge-compensation is shown in Fig. 52. The smaller wedges are fixed, and the large ones, as before, movable. The thick ends of the large wedges face in the same direction, so as to eliminate as far as possible, the displacement of an air layer between the wedges. Ordinarily, the wedge angles of the negative wedges are made, as nearly as possible, equal to those of the positive. As may be readily seen, it is possible with this combination to compensate negative as well as positive rotations. Its great advantage over the single wedge arrangement is found in the fact that it does not give the zero-rotation for a single position only of the large wedges as shown, for example, in Fig. 52, but for any position of the one wedges, a corresponding one of the other may be found for which the rotation is again zero. This follows from the fact that the thicknesses of the positive and negative plates are changed to the same extent by movement in the same direction A small rotation may, therefore, be compensated several times by choosing different parts of the large wedges, so that it is possible to largely eliminate wedge errors by taking the mean of these several determinations Other facts concerning double wedge-compensation can be brought out in the discussions of the following paragraphs.

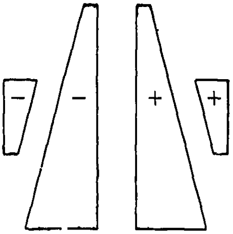

Fig 52

124. **Preparation of a Sugar Scale for Polariscopes with Circular Graduation.**—The following paragraphs deal with the sugar scale introduced into German saccharimetry by Ventzke, which is naturally the most important part of the saccharimeter. We enter upon a field in which, unfortunately, much uncertainty still exists, and in part must exist, since experimental investigations in this direction have not yet handled the subject with sufficient completeness or accuracy. For this reason, in the following, many points will be touched upon only briefly, and others not at all. Above all, it must be explained at the start, the method will not be indicated here which alone can lead to a scientifically unobjectionable sugar scale. Complete clearness and accuracy in this field can be expected only after the

conclusion of the extended investigations which have been undertaken by the Reichsanstalt.

It is important in practice to have a scale which shows directly in per cent the amount of sugar in the substance investigated. It will be assumed in all that follows, that a constant temperature of say 20° is maintained. Let a grams of pure sugar be dissolved in enough water to make a solution of exactly 100 cc. and then polarize the solution in a 20 cm tube of the Lippich polarimeter, using sodium light; let the observed angle be β. We shall consider a as the *normal weight* and designate the solution made as the *normal sugar solution* Next assume a solid or liquid substance which contains along with sugar, only such bodies as are inactive and soluble in water. In 100 grams of this substance let there be present p grams of pure sugar; then p is the percentage amount of sugar and the determination of this is the problem of optical saccharimetry. Dissolve now a grams of this substance in water, dilute to 100 cc and polarize as before in the 20 cm. tube, the observed angle is now γ. For aqueous sugar solutions the rotation is known to be proportional to the concentration; that is, to the number of grams in 100 cc. of the solution (as this is not absolutely true, the variations and corrections will be discussed later). As the concentration of the normal sugar solution is a, and that of the second solution $0.01\, a\, p$, then it follows that $\beta : \gamma = a : 0.01\, a\, p$, from which $p = \frac{100\, \gamma}{\beta}$, or also, $\beta : \gamma = 100 : p$; that is, the two angles of rotation are related, as are the percentage strengths of the original substances, the strength of the pure sugar being, of course, 100 per cent Now, if we take $\beta = 100$, γ will be equal to p, and in polarizing, we read directly the desired percentage strength. Therefore, in order to find the percentage amount of sugar in a substance, it is only necessary to polarize in a 20 cm. tube, a solution of the substance which contains the normal weight dissolved to make 100 cc As seen, this normal weight may be chosen quite arbitrarily; the length only of the sugar scale depends on it, as this is proportional to the normal weight We shall apply this sugar scale of the polarimeter now to the saccharimeters

125. Preparation of the Sugar Scale for Saccharimeters.—Let the analyzer of the polarization apparatus, using white light, be brought into the position of optical equilibrium and insert the single Soleil wedge-compensation between the analyzer and analyzer diaphragm, so as to be able to compensate the positive rotation of sugar solutions We assume the constant temperature of say 20°, and, for the moment, perfect equality in the rotation dispersion of sugar and quartz. Then let the large wedge be so moved that optical equilibrium still obtains, and at some convenient point on the setting of the large wedge make a mark to be designated as 0 This mark prolonged to the fixed framework of the mounting, gives the fixed index position. In this way the zero-point of the apparatus is determined. Then the normal sugar solution in the 20 cm. tube is inserted, and the large wedge is moved until optical equilibrium is secured again A second mark is now made on the large wedge, opposite the fixed index mark, and this is designated 100 In this manner, the extremely important 100 mark of the instrument, upon the accuracy of which everything depends, is established. If, next, the interval between the 0 mark and the 100 mark is divided into a convenient number of exactly equal divisions, the instrument is ready for use. As the displacement of the large wedge is exactly proportional to the amount of rotation of the inserted sugar solution, it follows that the percentage strength of pure sugar may be again read off directly on the scale. If the normal weight of a substance is dissolved in water, diluted to 100 cc , and if the solution is polarized in a 20 cm tube, the number read on the scale gives the percentage amount of pure sugar present.

Imagine next a positive quartz plate, perfectly plane parallel, and cut perpendicularly to the optical axis, and of such a thickness that it gives the 100 point in an accurately graduated saccharimeter. By the aid of such a plate, it will now be much easier to control the 100 mark of instruments than through the use of a normal sugar solution, the exact preparation of which requires the expenditure of much time. A quartz-plate so made is called a *normal quartz-plate*, and, as a matter of fact, all saccharimeters are in practice graduated by it. *Normal quartz-plates are to be defined, naturally, by their* *rotation and not by their thickness, because the latter cannot by any means be as accurately measured as the rotation.* It need hardly be remarked that saccharimeters may, of course, be graduated with quartz-plates which do not polarize exactly 100, as long as it is known to what value on the sugar scale they correspond.

126. **The Ventzke Sugar Scale.**—The normal weight has not been numerically defined in the preceding paragraphs, because it may be arbitrarily chosen, and in the course of time has been frequently changed At the present time, only two sugar scales are found in common use, the German or Ventzke scale, and the French scale, of which the first only will be discussed. The French scale[1] must be considered as quite unsatisfactory as its hundred point is defined by the rotation of a quartz-plate 1 mm in thickness. This use of the thickness of a quartz-plate in the definition of a sugar scale is not alone wholly unnecessary, but it is also very unpractical, because as often as the absolute rotation of 1 mm of quartz is differently determined, it is necessary to correspondingly change the normal weight; this explains why it is that the French normal weight has been changed at least once in every ten years.

Ventzke[2] proposed, first, a method for preparing the normal sugar solution, which was intended to render the use of a balance unnecessary. He defined as the normal sugar solution, a solution of pure sugar in water which should have at 17.5° the specific gravity of 1.100, referred to water at 17.5°. To determine then the polarizing sugar of any substance, it would be simply necessary to prepare a solution of it of this density by aid of an aërometer. But naturally this method could not give exact results, because the salts in the cane-sugars to be investigated have an effect, and have usually a density different from that of sugar itself; it was, therefore, soon abandoned. But as the 100 point of many saccharimeters had already been fixed by aid of the normal sugar solution of 1.1 sp. gr., and as it was not desirable to change the scale once introduced, the concentration of the Ventzke normal solution at 17.5° was then determined. Investigations showed that 100 cc. of such a solution contains 26.048 grams of sugar weighed in air with brass weights. The normal weight should be then 26.048 grams. If then this weight of pure sugar is dissolved to make 100 cc. and polarized in the 20 cm tube, the 100 point on the Ventzke scale is again found. As this method was in use long before the Mohr cubic centimeter was suggested, the number 26.048 must certainly have been applied to true cubic centimeters. After the introduction of the Mohr graduated flasks, the instrument makers, especially Schmidt and Haensch in Berlin, began to employ a solution of 26.048 grams of sugar in 100 Mohr cubic centimeters in fixing the 100 mark of instruments. For a number of years, then, the definition of the normal sugar solution has been this: *That sugar solution has the normal strength which contains at 17.5° in 100 Mohr cubic centimeters, 26.048 grams of cane-sugar weighed in the air with brass weights.*

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[1] The French scale is described in this way. That sugar solution has the normal weight whose rotation in a 20 cm tube is equal to that of a quartz plate 1 mm in thickness The normal weight thus defined has suffered many changes in the course of time, as it has varied between the limits, 16 02 and 16 471 gram. These two weights differ by about 2 8 per cent

[2] Ventzke Erdm Jour fur prakt Chem, **25**, 84 (1842), **28**, 111 (1843)

As the Mohr cubic centimeters have continually given rise to error, it was finally determined to go back to true cubic centimeters. This last definition of the normal sugar solution will then be changed so as to correspond to true cubic centimeters. The following is the definition of the Mohr cubic centimeter.[1] If 100 grams of water are weighed in the air with brass weights at 17.5°, the volume is 100 Mohr cubic centimeters. If we take into consideration, the weight of the air displaced in weighing and the specific gravity of the water at 17.5°, it follows that 100 Mohr cc. = 100.234 true cc.[2] Therefore, the definition of the normal sugar solution for true cubic centimeters is this A sugar solution has the normal concentration when it contains 25.9872 grams of cane-sugar, weighed in air with brass weights, dissolved in water to make 100 cubic centimeters at 17.5°. As again appears from the lack of agreement in the specific gravity of sugar, and the substances whose sugar content is to be determined, it would be necessary to reduce all weights to vacuo to secure a perfectly accurate result As the specific gravity of pure sugar is 1.6, the 25.987 grams in real mass is 26 003 grams. The normal sugar solution contains then 26.003 true grams of sugar dissolved at 17.5° to make 100 true cubic centimeters. But in what follows we shall retain the air weighings, as the error made by neglecting the reduction amounts seldom to 0.05 per cent., which has no importance in practice. Finally, it must be added that the variations in the normal weight from changes in the density of the air amount to about ± 0 0007 grams for 26 grams of sugar, and are likewise unimportant in practice.

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[1] Mohr Chemisch-analytische Titrirmethode, 44-50 (1886).

[2] The Mohr flasks made by the firm of Schmidt and Haensch hold, as experiments of the author show, in fact within ±0.03 per cent of 100.23 true cubic centimeters.

Retaining then the long established definition of the 100 point, the preparation of the Ventzke sugar scale, and the determination of sugar in a substance are as follows. *A normal sugar solution is made by dissolving 26.048 grams of pure cane-sugar, weighed with brass weights in air, in a 100 cc. Mohr flask at 17.5°, and this is polarized at 17.5° in a 20 cm. tube in the saccharimeter, care being taken to keep the wedge-compensation also at 17.5°; this establishes the 100 mark (100° V) of the saccharimeter Then by weighing and dissolving 26 048 grams of an impure sugar under the same conditions, and polarizing in the same tube, the compensation still at 17.5°, the Ventzke scale gives directly the amount of pure sugar in per cent.*

Now, in regard to the accuracy with which the saccharimeters in the hands of sugar chemists agree with this definition of the true 100 mark, nothing definite can be said[1] Certainty with reference to the accuracy of the 100 point on the Ventzke scale will be established by the investigations of the Reichsanstalt.

127. The 100 Point of the Saccharimeter.—Suppose the 100 point of a saccharimeter accurately determined by means of a correct normal sugar solution, and then a normal quartz-plate made which polarizes exactly 100° V in the so-graduated instrument. Then by aid of this plate, new saccharimeters may be much more accurately graduated than with freshly prepared sugar solutions. In the first place such a solution would always vary more or less from the correct normal solution; and, secondly, it would be only with the greatest difficulty that the normal temperature required by the definition could be maintained, especially in the quartz compensation. But the normal quartz-plate remains always applicable and correct, and its rotation in the saccharimeter is independent of the temperature, as long as care is taken to have the plate and compensation wedge at the same temperature, because the temperature coefficient of positive and negative quartz-plates is the same. For a long time, therefore, all saccharimeters have been graduated with such normal quartz-plates, which goes to explain the remarkable agreement in the 100 points of the instruments purchased from dealers.

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[1] The work of Nasini and Villavecchia (Sul peso normale pei saccarimetri, Pubbl. d. Lab chim centr d Gab 1891. Oesterr.-Ungar Zeitschrift f Zuckerindustrie, I Heft, 1892) adds nothing to the discussion

The 100 points on the saccharimeters made by Schmidt and Haensch in Berlin, which are now used in all parts of the world, seldom differ by more than 0.05 to 0.1° V, and the differences are usually smaller. It was, therefore, very commendable that the firm of Josef-Jan Fric in Prague, which also began the construction of saccharimeters, should bring their instruments into exact agreement with those of Schmidt and Haensch. How then may the 100 point on these saccharimeters be defined? This can be most simply done through the rotation of the normal quartz-plate for some definite light, as the sodium ray. Experiments by Schönrock[1] with four quartz-plates of about 100.3°, 93.5°, 91.7° and 75.4° V in a Schmidt and Haensch half-shadow saccharimeter, and experiments by Josef-Jan Fric[2] with a normal quartz-plate and a plate of about 99.7° V, in a large number of saccharimeters, have shown in complete agreement that the normal quartz-plate at 17.5° rotates the sodium ray 34.68° ± 0.02°.[3] It should be remarked that the quartz-plates and compensations were kept at the same temperature in the saccharimeters during the experiments, and that the result is independent of the composition of the white light used, as the differences for different lamps remained below 0.03° V. Therefore, we can take for quartz-plates:

100° Ventzke = 34.68 circular degrees for D at 17.5° C.[4]

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[1] Schönrock: Ztschr für Instrum., 16, 242 (1896)

[2] Personal communication to the author

[3] The optical center of gravity of sodium light = 589.3 $\mu\mu$

[4] Or, 100° V = 34.69° arc for D at 20°.

The number 34.68 is called the *factor of reduction*. If a quartz-plate is polarized in a saccharimeter with its temperature kept equal to that of the wedge-compensation, and if it shows a° V, then the quartz-plate will have a rotating power for sodium light equal to $0.3468\ a \pm 0.0002\ a$ circular degrees at 17.5°. More about the reduction factors for substances other than quartz, will be found in §129 and §153. If the rotation of a quartz-plate 1 mm. thick, at 17 5°, for sodium light is 21.714°, the thickness of the normal quartz-plate must be about 1.597 mm

The following may be said about the dimensions commonly chosen in the quartz wedge-compensations used in saccharimeters. The wedge angle of the quartz is usually taken at 3°, so that the distance between the 0 and 100 points on the scale is about 30.5 mm. The whole interval is divided into 100 equal parts, and by a vernier, one-tenth Ventzke may be read off In the simple wedge-compensation, the two wedges are usually positive, and the compensation plate negative and about 4.3 mm. in thickness. If the large wedge is then moved toward the 100 point, the thickness of the two wedges decreases

128. **Testing the Saccharimeter Scale.**—As the agreement of different saccharimeters at the 100 point leaves little to be desired, it may be asked now how the scale of a single instrument may be tested between the zero-point and 100 point The error in graduation in the scale and vernier should remain everywhere below 0.05° V. The ivory scales formerly commonly used have been abandoned, and properly, because their length is influenced by the moisture in the air, the changes amount to 0.3° V and more. The nickelin scales now commonly used are free from this error, and are also independent of changes in temperature as the change in length between 0 and 100, with a temperature fluctuation of 10°, is only about 0 01° V

Furthermore, the wedge should give correct results at all parts of the scale; that is, it should be so made that when it is moved through the nth part of the whole distance (100° V), the change of rotation produced in the compensation should be the nth part of the rotation of the normal plate corresponding to the 100 point on the scale This would be the case exactly if the large wedge were perfectly plane on both sides, optically homogeneous, and its motion without error. Errors in the construction and character of the small wedges and the compensation plate are of less importance as they are fixed in position, and because the wedge-compensation is close to the analyzer, while the polarizer is focused with the telescope; the rays from the whole field of view pass through the two small wedges and the plate and uniformly over their whole extent. As regards the large wedge, it is possible with sufficient care to make its surfaces so plane that the error occasioned here in the saccharimeters is inappreciable. As 0.1° V corresponds about to 0.0016 mm in thickness of the wedge, the notion has become common that the surfaces bounding the wedge cannot vary $^{16}/_{10\,000}$ of a millimeter from absolute planes, if it is to give readings correct to within 0.1° V; but as it is impossible to make the whole facing surfaces of the wedge, 30 mm. long, as perfectly plane as this, the errors often amounting to tenths of Ventzke degrees are supposed to be explained. But all of this is based on error; the consideration would be true only when a single ray were dealt with In reality, however, we work with a whole field whose length is about a sixth of the whole wedge-length If it is considered further that the wedge is placed right at the analyzer, it may be understood that a slightly convex or concave bounding surface on the wedge hurts nothing Errors are occasioned only when the radius of curvature has not a constant sign, that is, when points of inflection are present, but such surfaces are seldom met with. The optician can, in fact, prepare the wedge so that no errors need result from faults of construction Then how may it be accounted for that variations amounting to several tenths of a Ventzke degree are almost the rule? The answer to this question is simple, but not very encouraging. Nearly all errors which are found are due to the optical impurity of the quartz wedges[1] It must, unfortunately, be admitted that quartz is a very poor material, so that one rarely comes into possession of optically faultless plates of 1 to 2 square centimeters of surface; it must even be considered a piece of good fortune to possess a pure quartz-wedge 3 cm. long and of corresponding thickness. If now we examine the wedge compensations further in respect of their optical purity, it must seem in many cases impossible that with such material such delicate observations could be made, when the mean error of an adjustment is only about ± 0.03° V; yet this is the case with the half-shadow saccharimeters. This is explained by the fact that the wedge-compensation, fortunately, is located at the analyzer, so that its image, with a correct path of the rays, according to §96, coincides with the plane of the pupil of the eye and the impurity therefore cannot be recognized. Now, if the large wedge be moved new and different parts are then passed by the rays, and the rotations of these may differ considerably from each other.[1] But as the irregular parts of the wedges appear only gradually in the portion of the field occupied by the rays, the errors in a saccharimeter do not show sudden changes from point to point, but are subject to gradual variations, as the author has had opportunity of observing. Therefore, if the errors are determined for say 5°, 10°, 15° V and so on, and if these are plotted on coordinate paper, with the Ventzke degrees as abscissas and the errors as ordinates, it will be possible to find from the curve passed through the tops of the ordinates, the errors for any intermediate points. The simplest and at the same time the best method of finding errors is through the examination of different parts of the scale with good quartz plates. But as this is not always practicable for the individual owners of saccharimeters, other methods of error determination have been devised.

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[1] See "Die Thätigkeit der physikalisch-technischen Reichsanstalt" under Brodhun and Schönrock; Ztschr für Instr., 17, (1897).

Accurate results are alone furnished by the control observation tubes made by Schmidt and Haensch and described in §163. These give more accurate results than the preparation of a large number of solutions of proper rotation for the reason that in the control tubes, relative measurements only need be made as soon as the 100 point is once for all accurately determined. The control observation tubes are constructed on the principle of making the length of the rotating liquid column variable and the variation measurable. As the deflection of the plane of polarization is proportional to the length of the liquid layer, the rotation decreases in the same degree as the length of the column. The examination with the control tube is then made in the following manner: To avoid unnecessary corrections, the zero of the vernier is brought into exact agreement with the zero of the scale, using the vernier correction in aid of this Then the 100 point must be at exactly the right distance from the two zero points, which, according to §127, is nearly always the case. Then the control tube is filled with a sugar solution whose rotation is somewhat greater than 100° Ventzke, when the tube is pulled out to its full length The tube is then shortened until the rotation gives exactly $a = 100°$ V, when the length l is measured accurately If the conditions of experiment, and most important, the temperatures of the wedge-compensation and the sugar solution, are kept constant and the length of the tube then shortened to l', the rotation corresponding to this length is $b = a\,l'/l$. If instead of reading off b, the value read is exactly b_1° V, then the error in the immediate neighborhood of the point b_1 is given by $f = b - b_1 = (a\,l'/l) - b_1$, this error, f, is to be added algebraically to the observed value b_1, in order to obtain the true value of b_1 in Ventzke degrees In this way, the errors of any desired number of points on a considerable portion of the scale may be found, and the length of this is limited simply by the extent to which the tube may be shortened With a properly constructed control tube, using a single solution, it is possible to determine the errors from 100° V down to 55° V. Then the tube is filled with a new solution whose rotation, at full length, is something over 55° V, and the point 55° is taken as the new starting point, because its error has been already determined, and then observations are made as before until the error at the 5° mark is reached. The following table shows how, with five different properly chosen solutions, the errors on the whole scale may be found:[1]

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[1] The author once had the opportunity of examining two plane parallel quartz plates about 5 mm. thick and well made, which, when polarized in a half shadow apparatus with sodium light and large half shadow, that is, with rather bright field, gave pretty constant results, but when the plates were turned in their planes the angles of rotation assumed all values between 0° and 90°. Although quartz-wedges of corresponding bad quality could hardly be found, it cannot be denied that the error of a saccharimeter must be largely ascribed to the optical impurity of the wedges.

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[1] Absolutely pure sugar is not necessary for the purpose

The tube length variable between 42 cm and 22 cm

Cane sugar solution		Starting point °V	Errors found at the points
No.	Concentration, or number of grams of sugar in 100 cc of solution		
1	12 53	100	95, 90, 85 ... 60, 55
2	6.89	55	50, 45, 40, 35, 30
3	3.76	30	25, 20, 16
4	2.00	16	15, 10, 9
5	1.13	9	5

Of course, the accuracy of the tube scale itself must have been previously determined. By plotting the errors of the saccharimeter scale on coordinate paper the error curve is found. As may be readily seen, this method of finding errors, in case it is expected to give really accurate results, requires quick and very close work. It is, therefore, recommended to make on different days two complete series of determinations to secure a picture of the accuracy obtainable If this is satisfactory the mean curve is taken as the final one. *Although the testing of a saccharimeter scale requires some pains, one should not hesitate to do the work, because the errors remain constant and are absolutely independent of time so long as no injury has happened to the optical mechanism of the instrument. An error curve once accurately established holds good always.*

We turn now to a consideration of the double wedge-compensation of Schmidt and Haensch (§123) on the value of which different views have been held. The zero point is usually found at the thinner end of the long wedge, so that the working wedge is negative and the control wedge positive To avoid unnecessary zero point corrections the control wedge is placed exactly at 0 and optical equilibrium is secured by moving the working wedge , if the zero point of the working scale does not coincide exactly with that of the vernier the difference is corrected as before by means of the micromete screw below the vernier corresponding to the scale. Then th working wedge is placed at 100 and a test is made as accuratel as possible of the correctness of the 100 mark. If now optica equilibrium is again established by aid of the control wedge this should stand exactly at 100. If this is not the case the scale has been carelessly made, and the apparatus should be simply sent back to the manufacturer. Naturally the two scale lengths are usually not the same, which is not necessary. If the two wedges are accurately made it must follow that when one of them is put on any point of its scale optical equilibrium must obtain when the other is placed at the same point on its scale. If in this way the two wedges are tested from 5° to 5° and if the differences in readings actually remain below 0.03° V., it may be said with great probability that the wedge-compensation does not possess any appreciable error, because it would be by extraordinary chance that any errors due to optical impurities in certain places in one wedge would be exactly compensated by corresponding errors in the other. In addition to all this, in order to be certain, it is well to test at least a few points by aid of the control tube. As a rule, however, it will be found in testing the two wedges as above that the differences in the readings in certain parts of the scale amount to some tenths of a Ventzke degree, so that an accurate determination of errors is here also required For this purpose the reading differences from 5° to 5° V. must be accurately found in this way. The control wedge is placed at 95° exactly, and five adjustments at optical equilibrium are made with the working wedge, from which the mean is taken and subtracted from 95, to give the reading difference In this way results are obtained down to the 5° mark Then the whole series of observations is repeated by placing the working wedge exactly at 95° and so on, and securing optical equilibrium by aid of the control wedge The two series of observations should give the same differences with opposite signs, within the limits of errors of experiment, which is to be remembered, in general, in all error corrections From each two corresponding differences the mean of the absolute values is taken which is to be used in the further calculations, with proper sign attached. The control wedge is next placed exactly at 0 and the complete determination of errors in the working wedge is made by use of the control observation tube as fully explained above. From the curve of errors for the working wedge and the table of adjustment differences for the two wedges the error curve of the control wedge may be found in a way easily recognized. The latter may be found also directly by aid of the control tube and positive sugar solutions, by placing the working wedge at exactly 100 and finding the errors in the control wedge from 5 to 95. This furnishes, at the same time, the best control of the accuracy of all the observations made. If now the rotation of a solution is found with one wedge and controlled, after taking out the solution, with the other wedge, then after adding the corrections from the error curves the two wedges should give exactly the same result *It follows, therefore, that correct observations may be made with the double wedge combination and an actual complete control secured only when the error curves of the two wedges are known It appears, therefore, that as accurate work may be done with the single as with the double wedge-compensation.*

129. **Observation of Solutions in the Saccharimeter.**—In the following considerations we shall keep the half-shadow saccharimeters in mind as they have completely displaced the color instruments. As the rotation dispersion of sugar does not agree absolutely with that of quartz, a slight but unimportant difference in the colors of the field of view is found in testing high polarizing sugar solutions. Although this does not interfere with the accuracy of the reading for a practiced observer, the adjustments of different observers with different degrees of color sensitiveness, may vary considerably from each other To eliminate the colors either a plate of potassium dichromate or a cell with solution of potassium dichromate is placed between the light and illuminating lens , a dichromate plate in the ocular is not used As regards the changes in the rotation of sugar solutions for white light of different kinds of lamps it is found that appreciable differences occur only when observations are made at one time with, and at other times without, dichromate plates.[1] Still this point requires fuller systematic investigation. With reference to testing the saccharimeter scale by aid of the control tube it must be further remarked that the illumination must not vary during determination of the curve of errors. The curve finally found is, however, independent of the illumination, as the error in the 100

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[1] Ztschr fur Instrum , 16, 243 (1896)

point is placed equal to zero. If a change is made from one light to another, and a change in the 100 point follows, that is, if the rotation of a normal sugar solution varies by *a*° V., then in a corresponding manner the point *b* of the scale would change by 0 01 *a b*° V.

As complaints about continuous changes in the zero points of instruments are still heard in practice, reference must be again made to §96 These changes may be very easily avoided. The focal length of the illuminating lens must be chosen so as to be equal to half the distance between this lens and the analyzer diaphragm, and the source of light is placed as far away from the illumination lens as the latter is distant from the analyzer diaphragm, or better so that after putting the absorption cell in position a sharp image of the source of light will be thrown by the illuminating lens on the analyzer diaphragm. If this is the case observations may be made day after day without disclosing the slightest change in the position of the zero point, since in the saccharimeters the polarizer and analyzer are fixed in definite positions, or at least should be; a lateral displacement of the source of light cannot be followed by a zero point change.

If the Ventzke reading in the investigation of a sugar solution is to be converted into circular degrees referred to sodium light, this may be done as explained in §127 by aid of the reduction factor 0 3468, although this properly applies to quartz plates only An absolutely accurate conversion is not always possible, because of the effects of temperature and the variations in the rotation with the illumination and color sense of the observer Landolt[1] has actually found in the observation of a cane-sugar solution in a Schmidt and Haensch half-shadow saccharimeter, with a gas lamp, that a rotation of 100° V corresponds to the rotation of 34.65° ± 0 05° for sodium light. But if it is required to accurately measure the rotation of a sugar solution for sodium light this must be done in a polarimeter actually illuminated by sodium light.

130. Effect of Temperature on the Saccharimeter Reading.—In order to give an idea of the error which results through temperature changes in the determination of cane-sugar the errors from several sources will be discussed on the basis of a temperature variation of 10° In the saccharimeter itself the wedge-compensation only is variable with the temperature; the zero point is constant, but all other points change in value As we can take the temperature coefficient of quartz (and sugar also) as constant through the interval considered, for all wave-lengths, that is, the rotation dispersion as independent of the temperature, a simple calculation shows that a temperature variation of 10° changes the 100 point (100° V.) about +0.15° V From this it will be recognized that the temperature of the compensation must be pretty accurately known if one expects to polarize within a few hundredths Ventzke[1]

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[1] Landolt: Ber. d chem Ges 21, 194 (1888)

Now let us consider the polarization of a cane-sugar solution in the saccharimeter, and in order to have a definite case in mind assume that we have a normal sugar solution in a 20 cm. tube, which must therefore polarize about 100° V. If the tube is of glass its length will increase with the temperature, and, therefore, the rotation of the sugar solution also. A temperature elevation of 10° corresponds to a change of +0 01° V, therefore, the change from this cause is inappreciable in observations. But at the same time the concentration of the solution decreases with the increase in temperature, and the rotation must therefore decrease. As the coefficient of expansion of a normal sugar solution at about 20° is 0.000291, the increase of temperature through 10° produces a change in rotation of —0.29° V. Besides this the specific rotation of cane-sugar decreases with increase in temperature, so that the angle of rotation still further decreases; the older observations of Tuchschmid, Seyffart, and Andrews, which gave the specific rotation of cane-sugar as constant at different temperatures, are not correct, since the decrease in rotation with increase in temperature is even quite appreciable[2] On account of this change in specific rotation the rotation of the normal sugar solution is decreased about —0.21° V. more by the 10° increase in temperature The whole change then is about —0.50° V. From this it is seen how necessary it is to control the temperature in exact work. It must be further noticed that the errors due to the wedge-compensation and the sugar solution are to be added to each other, as indeed the rotation of quartz increases while that of sugar decreases with increasing temperature, so that the whole error of the polarization of the normal sugar solution will be 0.65° V. *If now it is expected to determine the 100 point of a saccharimeter to within ±0.03° V. by aid of a normal sugar solution, then, aside from all other sources of error, and especially those in the preparation of the solution (temperature again!), the temperature of the compensation and of the solution in the tube should not differ from that in the definition of the 100 point by more than 0.5° C* Now, at least, one should be able to recognize how difficult the graduation of a saccharimeter by aid of a normal sugar solution really is. As further, the mean adjustment error of the present half-shadow instruments is only about ±0.03° V., and as these saccharimeters are used only in technical work there would be no sense in increasing their delicacy still further, since, at the present time, polarizations are made with a degree of accuracy which is wholly illusory.

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[1] As regards the temperature of the wedge-compensation we are very much in the dark with the present constructions, as the temperature of the rather thick wedge and compensation plates follows variations in the room temperature very slowly It may, therefore, be recommended to place the compensation box in a confined space enclosed by non-conducting materials and have a thermometer, graduated in whole degrees, extend into the box It is also well to have the light passing into the apparatus and that reaching the reading mirror also pass through a cell filled with water to absorb the heat rays and yield a cold light

[1] See "Die Thatigkeit der physikalisch-technischen Reichsanstalt" under Schönrock, Ztschr fur Instrum, 17, (1897). [But, contrary to the statement in the text, this was previously accurately pointed out by Andrews, Technology Quarterly, May, 1889 p 367 See also later, under Constants of Rotation Tr]

1 The Soleil-Ventzke Saccharimeter.

131. **Description of the Instrument.**—In the description of the different saccharimeters to follow, we shall be very brief, since it is only necessary to add a wedge-compensation to any one of the polarimeters described above to have the corresponding saccharimeter. As explained, the first saccharimeter was made by the Paris optician, Soleil, and was later improved by Soleil and Duboscq. This is the so-called color saccharimeter, and is shown in Fig 53 It may be made by setting the Robiquet polariscope, described in §100, at the position of optical equilibrium and then inserting a simple wedge-compensation between polarizer and analyzer. The light, therefore, passes the following parts in going through the apparatus from right to left; first, the regulator of the sensitive tint not described

above under the head of the Robiquet apparatus, and which must be referred to here, consisting of a nicol, A, which may be rotated, and a right or left quartz-plate, B, which is ground perpendicular to the axis, the illuminating lens C, the polarizer D, the Soleil double plate E, the wedge-compensation F, the analyzer G, and the telescope H. As in the Robiquet apparatus, adjustment is made on the transition tint by movement of the long wedge; that is, uniform color of the two fields is secured In §102, the drawback of the Robiquet instrument, that after inserting the rotating substance the transition tint no longer has the same color observed in finding the zero point, is referred to This fault appears in much less degree in the saccharimeter because the rotation dispersion of the active substance is largely compensated by the quartz wedges But, in order to keep the shade of the transition tint as nearly the same as possible after putting in the active substance, even if somewhat colored, and in order to give the observer the power of choosing the shade for the transition tint, for which the eye is the most sensitive, the so-called regulator has been added to the saccharimeter The light polarized by the nicol A passes into the quartz-plate B and suffers rotation dispersion, and on account of this, and the relation of the position of A to B, certain rays will not pass through the latter, or will pass with diminished intensity. By rotating the nicol A, the tone of the transition tint may, therefore, be changed at will

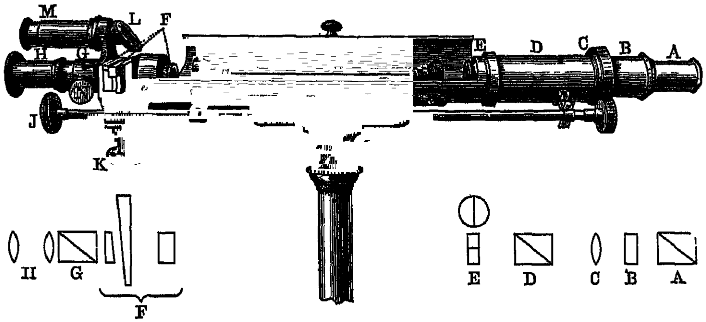

Fig 53

The rotation of the tube which contains the regulator A B is accomplished by aid of a spur-wheel and pinion, the latter being worked by a rod attached to the button J The brass frame holding the large wedge may be moved horizontally, and for this purpose is furnished with a lateral rack in which works a pinion wheel controlled by the button K. An inclined mirror, L, serves in reading the Ventzke scale, the image of the scale being thrown into the tube M which contains a magnifying lens. In the illustration, a screw is shown at N by aid of which the analyzer may be turned and brought into the proper position with reference to the polarizer ; this movement must be made, however, only by the instrument-maker in adjusting the apparatus, so that the observer has nothing to do with the screw N As regards the use of the instrument, reference is made to §97 and §102 The mean error of a reading is about ± 0.2° V.

As the adjustment to equality, of tint in the field of view is not possible with color blindness, inaccurate with deficient color sense, and for most eyes much more tiresome than the adjustment to uniformity of illumination, the much more sensitive half-shadow instruments have properly displaced the color instruments completely It is quite in vain to attempt to make the color instruments more sensitive by giving a concentric form to the Soleil double plate, the part of these in saccharimetry has been played and for good

2. *Half-Shadow Saccharimeters*

132. Construction of the Instruments.—The half-shadow polariscopes contain, always, an illuminating lens, a polarizing mechanism, the analyzer, and a telescope. In the construction of saccharimeters, the following polarizing arrangements are usually employed. The firm of Schmidt and Haensch uses, in general, the Jellett polarizer (§109) for the saccharimeters with double field, the double field Lippich polarizer (§114) could, of course, be applied as well In the saccharimeters with triple field, the triple Lippich polarizer is employed (§115). If, now, either kind of polarization apparatus is adjusted to uniform shadow on the fields of view, and a simple or double wedge-compensation is introduced between the analyzer and the analyzer diaphragm, the corresponding half-shadow saccharimeter is produced. The light passes then through the following optical parts: the illuminating lens, polarizing mechanism, wedge-compensation, analyzer, and telescope Polarizer and analyzer must have a fixed position and be properly protected against any accidental displacement, as is the case, for example, in all the instruments made by Schmidt and Haensch It must be considered an error of construction to give a saccharimeter a variable half-shadow. The zero point of the instrument varies naturally with the half-shadow. This should be made 5° to 8°. The mean error of an adjustment for a saccharimeter with double field is about ± 0 06° V, and for the saccharimeters with triple field, about 0 03° V.

Below a very condensed description of the commonly used types of saccharimeters will be given, with especial consideration of the mechanical construction.

133. **Half-Shadow Saccharimeter with Single Wedge-Compensation and Double Field (Schmidt and Haensch).**—This apparatus is shown in Fig 54 The movable quartz wedge is mounted in a frame attached to a lateral rack in which a pinion wheel controlled by the button A works. The reading of the scale and vernier is accomplished by aid of the inclined mirror in B, and lens in the tube C

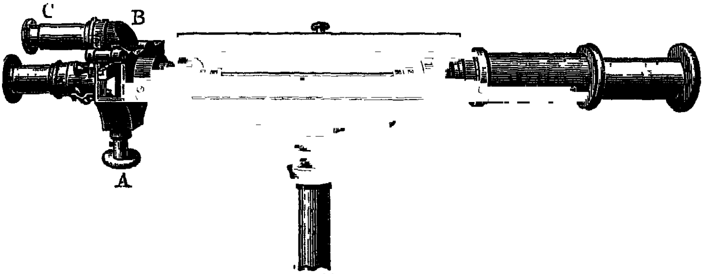

Fig 54

134. **Half-Shadow Saccharimeter with Double Wedge-Compensation and Triple Field (Schmidt and Haensch).**—In this instrument, shown in Fig 55, the black set screw A moves the working wedge while the yellow screw B moves the control wedge, and in such a manner that by aid of the lens C, the working scale is seen above and the control scale below. As regards the illumination of the scales this is accomplished by means of the

mirror D, which is attached to the ball and socket mechanism at E, and which may be so turned as to receive light from the

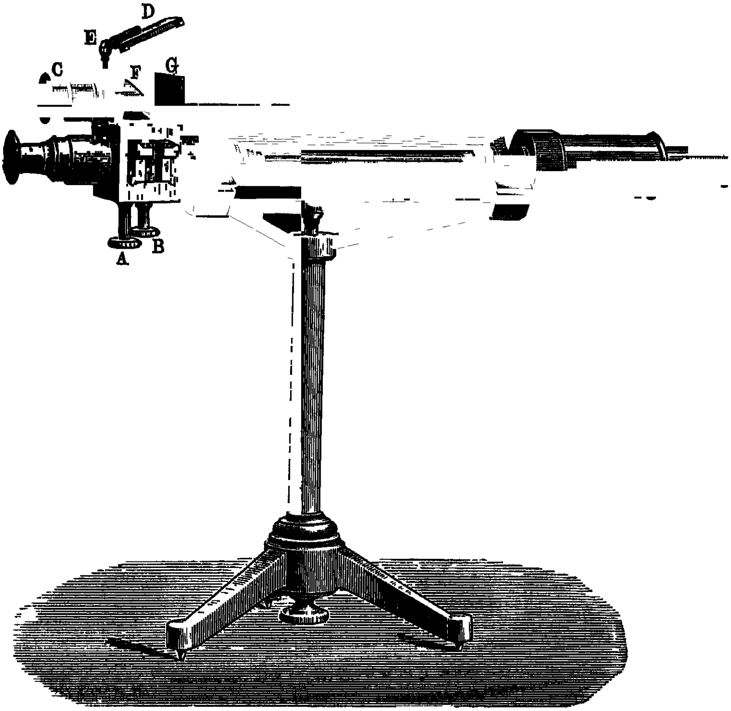

Fig 55

illuminating lamp and throw it through the matted upper surface of the glass plate F on the scales The small screen G serves to protect the scales from outside lights

135. **Beet-juice Saccharimeter with Limited Enlarged Scale.**[1]— This instrument, the front part of which is illustrated in Fig. 56, was constructed by Schmidt and Haensch from a suggestion of Stammer. It is distinguished from the previously described instruments only by its limited scale extending from 0° to 35° V. A reading of higher degrees is not necessary, since it is used only for the determination of sugar in beets. In order to carry out the polarizations in such cases, where in a short time the largest possible number of tests must be made, and

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[1] Stammer: Ztschr für Rübenzucker-Ind, **37**, 474 (1887). Schmidt and Haensch *Ibid.*, **43**, 1040 (1893)

to avoid the delay of reading by the telescope, the instrument is furnished with an enlarged scale which permits an easy reading to 0.1 of 1 per cent. with the unaided eye, and even at a distance. The mechanism consists of a segment of a circle attached in upright position to the wedge-compensation, and on which the beet-juice graduation of 0° to 35° V is marked. In the center of the segment there is a small drum, *R*, which is kept in position by a spring , this drum is attached to the movable wedge by a thin steel chain in such a manner that when the wedge is moved to and fro by the button *K*, the drum *R* is brought into motion, and then the long pointer joined to it moves over the graduation of the segment If the diameter of the drum bears a certain relation to the length of the movable scale, then the circular segment graduation gives exactly the whole and tenths of per cent. of the scale

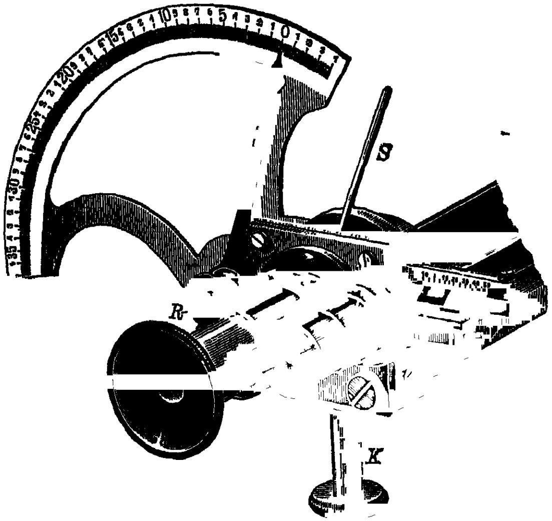

Fig 56

To secure accurate adjustment the apparatus is brought to the point of half-shadow uniformity ; if the scale then does not begin at 0° a correction is made by a key to be attached to *V*. In this position the pointer of the circular graduation should stand at 0° also ; any necessary correction of this zero point may be made by a slight movement of the small screw fastening the chain to the wedge, which is accomplished by aid of the little set lever *S*. Any movement of the wedge expressed in per cent. must be exactly duplicated on the circular graduation. If this is not the case a correction is made by turning the nut attached to *R* a little on or off, which has the effect of slightly increasing or decreasing the diameter of *R*, and, therefore, of making the deflection of the pointer less or more, to correspond. The whole adjustment must be revised from time to time.

136. **The Half-Shadow Saccharimeter of Peters.**[1]—This instrument, shown in Fig 57, is distinguished from the foregoing in several points which will be explained. It is a half-shadow saccharimeter with Lippich polarizer and double wedge-compensation, and is supported on two unusually stable feet, which prevent upsetting the instrument In the brass shell A, there is a wide glass tube with end plates, like a polarizing tube, which may be filled with a solution of potassium dichromate. The pointer at B is used to turn one of the nicols of the Lippich polarizer ; the scale is placed below here in order

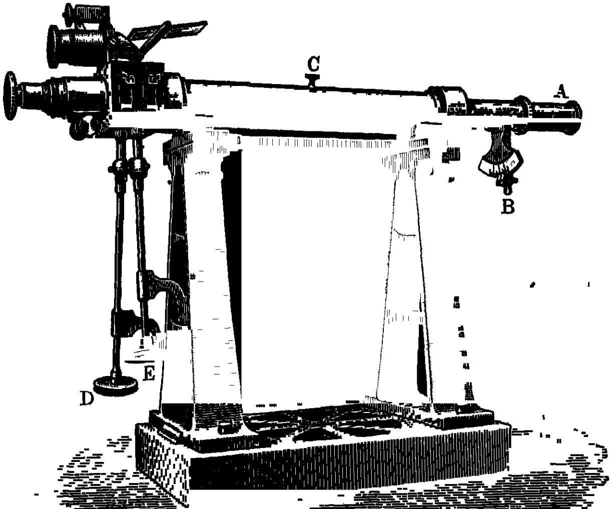

Fig 57

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[1] Peters (Berlin) Ztschr. für Rübenzucker-Ind , 44, 221 (1894)

to be able to illuminate the Ventzke scale above by mirror reflection from the polarization lamp. The pointer at B is usually left in a fixed position and can be moved only by aid of a special key. But this possibility of regulating the half-shadow is without value in a technical instrument and may give rise to serious errors; for as often as the index B is moved the analyzer must also be turned to the point of equal illumination of the two halves of the field; the technical saccharimeters must have, beyond question, a fixed half-shadow. The apparatus has no lid at C, but closing is effected, after laying in the observation tube, by rotating a movable, half-open shell The final adjustment screws are extended by means of universal joints so as to reach nearly to the table on which the apparatus rests, which makes it possible to move the compensation without lifting the arms. The screw D, which works the right scale, is placed somewhat lower than E, which turns the left one, so as to avoid possibility of confusion.

137. **Half-Shadow Saccharimeter of Josef-Jan Fric.**[1]—This instrument with double wedge-compensation, the front part of which is shown in Fig. 58, is distinguished from the ordinary constructions in this that each one of the two scales is read by a special lens and

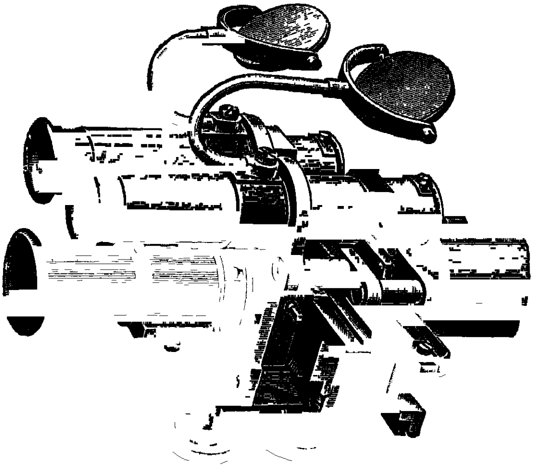

Fig 58.

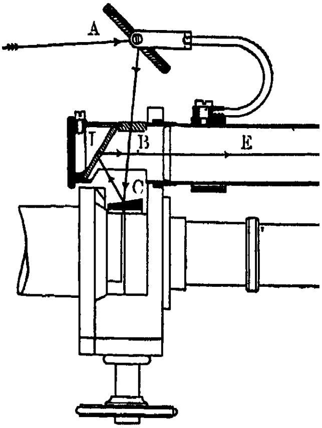

Fig 59

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[1] Joseph-Jan Fric (Prague) Oesterr-Ungar Ztschr fur Zuckerindustrie, V Heft (1895) E H Sargent & Co, Chicago, are the American agents for these new instruments

illuminated separately by a new and excellent arrangement, the details of which are shown in Fig 59 diagrammatically. The light coming from the regular illumination lamp is reflected by the movable mirror A and passes through the milk-glass plate B upon the scale C, the surface of which is so inclined toward the mirror D, that the light reaching the latter is thrown in the direction of the optical axis of the telescope E. The so illuminated metallic scale C appears on account of the diffuse light from the milk-glass plate, as distinct as the old ivory scales The left telescope with black mountings reads the working scale, while the right one with red mountings reads the control scale. Besides this, the control scale is seen by red light, since the milk-glass plate in this case is replaced by a plate of red glass, to exclude possibility of mistake in reading.

c. Illuminating Lamps.

1. Lamps for White Light

138. **Schmidt and Haensch Gas Lamps.**—Great importance need not be attached to perfect uniformity in illumination as long as a correct passage of the rays through the apparatus is provided for according to §96 and §129. Changes in the intensity of the light bring about no changes, then, in the zero point, and it is immaterial whether we use a flat burner or a round one. A very convenient form of lamp is shown in Fig. 60, which employs gas, and is furnished with a triple flat burner, metallic chimney and a reflector. As these gas and petroleum lamps are usually still furnished with a so-called condensing lens which, as a matter of fact, has no importance,[1]

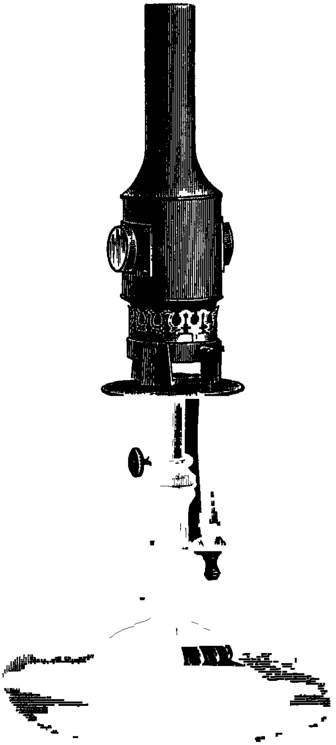

Fig 60.

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[1] The lens does not increase the intensity of the illumination, and always interferes with the correct passage of the rays

in ordering a lamp one should be careful to secure a form which has in place of this lens a clear glass plate.

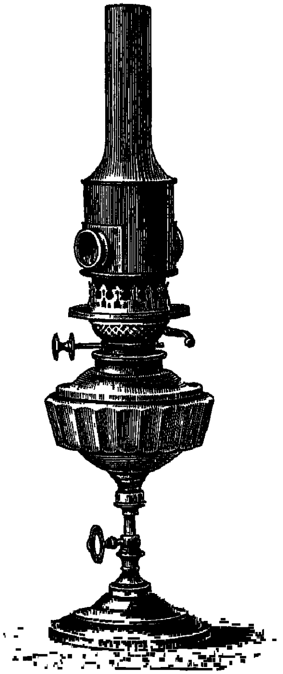

Fig 61

139. **The Hinks Petroleum Lamp.**—For use with petroleum, the Hinks duplex lamp with metallic chimney, shown in Fig. 61, has given excellent satisfaction. Before lighting the lamp, the precaution must be taken to see that the cap used to extinguish the flame is shoved back into its proper place, by aid of the lever on one side of the burner, so as to leave the wick perfectly free to burn evenly.

140. **Lamps with the Welsbach Incandescent Gas Light.**—On account of their intense light these can be strongly recommended for the illumination of saccharimeters For this purpose the ordinary lamp with glass chimney is furnished with a second outer chimney of porcelain or asbestos, which at the proper point is provided with a suitably large opening to permit the passage of the light. The polariscope is naturally directed toward the brightest part of the glowing substance. It is not at all necessary to use a ground-glass chimney, as, with proper distance between lamp and instrument (§129), the meshes of the mantle do not disturb in the slightest degree, since, in fact, the image of the glowing body produced by the illumination lens is formed at the analyzer diaphragm

141. **Lamp for Electric Light.**—This consists of a stand with the necessary connecting wires on which a very strong incandescent lamp (of about 50 Hefner units with 100 to 110 volts) can be moved in vertical direction. The metallic cylinder surrounding the globe has an opening in the right place to allow the best part of the light to pass

142. **Zirconium Light.**—The zirconium light is, by far, the

most intense white light. To produce it a Linnemann burner fed by oxygen and illuminating gas is used, the hottest part of the flame being directed against a plate of zirconia in a platinum support.[1] Instead of a zirconia plate a cylinder of the same substance may be used.[2] It is most advantageous to place the burner in a large sheet-iron box provided with windows, a door, and an inclined chimney. The lime light burners, fed by illuminating gas and oxygen, may also be strongly recommended [3]

2. *Lamps for Homogeneous Light*

143. **Simple Sodium Flame Gas-Lamps.**[4]—In order to secure a sodium flame of considerable duration, the lamp illustrated in Fig. 62 may be used This consists of a Bunsen burner which may be adjusted in vertical position, over which a metallic chimney is placed. The gas entrance, *s*, is found at one side where it will not become clogged by bits of salt dropping from the flame The chimney may be adjusted by aid of the screw *h* at the proper height. At the top of the column, *p*, which may be rotated, a rod is attached horizontally which carries at its end a bundle of fine platinum wires. These are so bent that they form a little pointed spoon. If this is filled with well dried salt and turned so as to rest in the front side of the flame, the melted salt is drawn up into the point of the spoon and produces an intense yellow light on volatilization. By aid of the sheet metal shutter *k*, which has an opening, the light from the

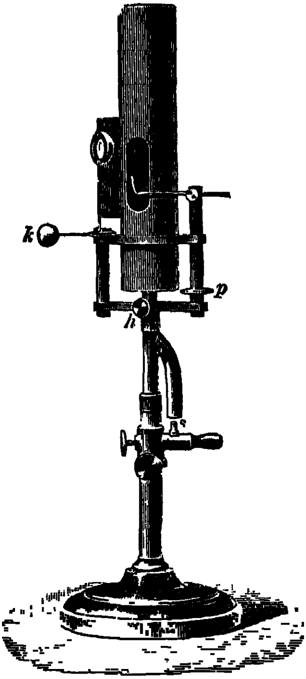

Fig 62

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[1] Linnemann "Ueber ein neues Leuchtgas-Sauerstoffgeblaesse und das Zirkonlicht," Wiener Sitzungsberichte II, 92, 1248 (1885).

[2] From M Wolz, in Bonn

[3] From Meckel, Kaiserstrasse 32, Berlin.

[4] From Schmidt and Haensch, Berlin.

brightest part of the flame only may be allowed to pass

A second sodium lamp, which is very much like the first, is shown in Fig. 63; the application will be readily understood. Instead of salt, well calcined sodium carbonate may be used in these lamps, the volatilization is slower, but the intensity of the light, at the same time, less

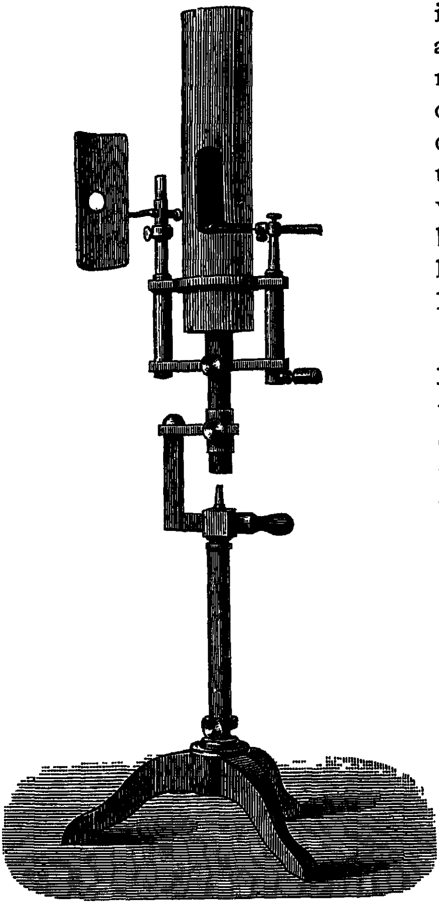

Fig 63

144. Pribram's Sodium Lamp.[1]—If it is necessary to work a long time with constant illumination, the Pribram lamp, shown in Figs 64 and 65, is found useful The gas led in at a emerges through the fine openings at b and mixes in the burner top c with the air which enters at d, the flow of which may be regulated by turning a perforated disk by aid of the lever k. The gas is ignited at the gauze top of the burner at e. The chimney b, which is lined with asbestos, has four openings, through one of which, m, the light reaches the polariscope, while a second one, i, is furnished with a cap and serves for igniting and observing the flame. At g and h two little platinum boats, which are filled with fused salt, may be introduced into the flame.

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[1] Pribram "Ueber einen neuen Brenner fur Natriumlicht," Ztschr anal Chem., 34, 166 (1895), made by Schmidt and Haensch

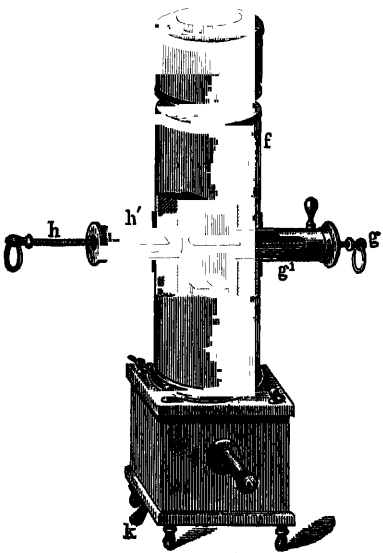

Fig 64

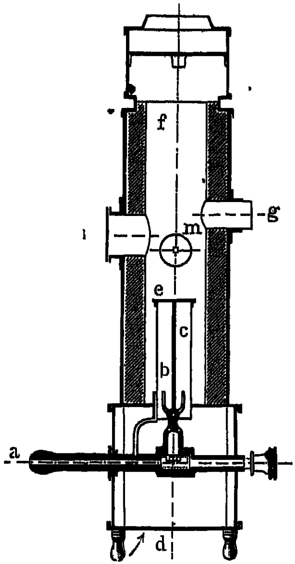

Fig 65

145. **Landolt's Sodium Lamp.**[1]—A much stronger sodium light than that furnished by the burners described may be secured by the lamp shown in Fig 66 A Muencke burner (Bunsen lamp with conical wire gauze top and so strong an air supply that the inner dark cone of the flame disappears) is supported on an iron stand, the upright rod of which carries a square chimney, B, made of sheet iron The front side of this chimney has a round opening, over which the plate C, with three holes of 20, 15, and 10 mm. diameter, may be shoved Two nickel wires, D, are laid across the sheet metal cylinder at the top of the lamp A, resting in notches in the cylinder, and around the middle of these wires pieces of nickel gauze are rolled The meshes of this gauze are filled with salt, and most easily, as shown in Fig. 67, by laying them in a little trough of nickel foil in which the salt has been previously melted by aid of two Terquem burners. By placing the cylinder of the Muencke burner low, so that the salt is just over the wire gauze cone of the lamp, a very intense color is produced at the front and back of the flame.

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[1] Landolt "Natriumlampe für Polarisationsapparate," Ztschr für Instrum , 4, 390 (1884), made by Muencke, Berlin.

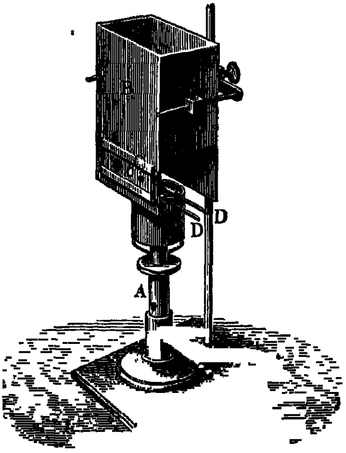

Fig 66

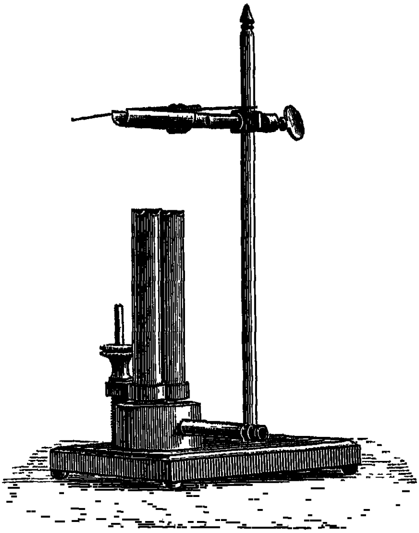

Fig 67

If instead of common salt dried sodium bromide is used, following the suggestion of Fleischl v. Marxow,[1] a very much more intense light is secured ; but the sodium bromide volatilizes much more rapidly than the chloride and bromine vapors escape from the flame In working with sodium bromide one must, therefore, place the burner under a good draft, as otherwise the polariscope may be completely ruined by the bromine vapors

146. **Intense Sodium Light.**—A very high illuminating power is found in the pencils suggested by du Bois,[2] consisting of sodium bicarbonate and sodium bromide in gum tragacanth, heated in the Linnemann oxygen blast-lamp As these pencils give out bromine vapors, a good draft must be provided Besides this, the greatly increased illuminating power calls for a great consumption of material, so that a rod about 4 mm. thick and 14 cm. long is completely burned in about ten minutes. If one wishes, therefore, to work with these pencils, it is necessary to have an assistant or a clock-work mechanism to continually regulate the flame. These drawbacks are avoided by using, according to Gumlich,[3] rods of fused sodium

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[1] Fleischl v Marxow Wied. Ann , 38, 675 (1889)

[2] Du Bois : Ztschr für Instrum , 12, 165 (1892)

[3] Gumlich *Ibid* , 16, 111 (1896).

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carbonate about 6 mm. thick and 15 cm. long in the Linnemann oxygen blast-lamp. No objectionable vapors are produced, and the rods burn so slowly that in a period of about seven minutes it is usually not necessary to change their position. Although the intensity of the light produced is not quite equal to that from the du Bois pencils, it is quite sufficient for nearly all purposes in polarimetry. As, furthermore, the use of these soda pencils is quite cleanly, the volatilization of fused rods in the oxygen lamp may be strongly recommended.

3. *Purification of the Sodium Light Optical Center of Gravity*

147. Lippich's Sodium Light-Filter.[1]—In the following considerations, in order to have a specific kind of instrument in mind, we shall assume that all observations are made with a Lippich half-shadow apparatus with double or triple field As the following paragraphs will take up also the comparison of polarimetric measurements, it may be remarked at the outset that the discussion can not be a complete one, because, in the first place, the limits of the book would not justify it, and, secondly, because in many cases it would not be possible to verify theoretical considerations by experimental data available

Assume a substance having the power of rotating the plane of polarization and kept under constant conditions It will then rotate lights of all wave-lengths through definite angles, depending only on these wave-lengths Let the rotation β correspond to the perfectly homogeneous light of wave-length λ. Now, suppose the apparatus illuminated by mixed light made up of light of wave-length λ_1 and light of wave-length λ_2 Let λ_1 be smaller than λ, and λ_2 greater than λ, but so nearly the same that the eye may not recognize the difference in shade between them. Notwithstanding the consequent rotation dispersion, it will then be possible to find the angle of rotation β_1 of the substance for this mixed light, as well as if the instrument were illuminated with perfectly homogeneous light. The same angle of rotation, β_1, would be found by using for illumination, a perfectly homogeneous light of wave-length λ_3. *It may be said, therefore, that for polarimetric measurements, λ_3 is the optical center of gravity of the mixed lights of wave-lengths λ_1 and λ_2; that is, if this mixed light be employed, rotations are obtained which actually correspond to the wave-length* λ_3. As all polarimetric measurements depend finally on comparisons of brightness, it may be recognized directly that the optical center of gravity λ_3, depends not only on the wave-lengths λ_1 and λ_2 but on the intensities of the two homogeneous components. For a definite condition of brightness in the two components we have, for example, $\lambda_3 = \lambda$ and consequently $\beta_1 = \beta$, if now, the brightness of the component λ_1 increases, then the optical center of gravity λ_3 will approach λ_1 from λ. *It may be now shown that the optical center of gravity λ_3 depends simply and alone on the wave-lengths and degrees of brightness of the two homogeneous components in the source of light, and not on the rotation dispersion of the investigated substances, or on the amount of the angle of rotation or the size of the half-shadow angle chosen, as long as the observations are made with the Lippich apparatus, and the absorbing power of the substance is relatively the same for the two components* In investigating substances with considerable color, care must be taken to see that this last condition is fulfilled , in what follows, uniform absorption is assumed.

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[1] Lippich Ztschr. für Instrum., 12, 340 (1892)

If we pass now to the general case, that is, if we assume that the source of light furnishes light of all wave-lengths, then, for polarimetric purposes, a definite optical center of gravity will correspond to this light also, as long as the field of view possesses the same color when the point of optical equilibrium is found with the observed substance in position, as it had at the time of the zero-point determination If this is not the case, then the optical center of gravity depends on the color sense of the observer, and the adjustment for reading becomes more and more inaccurate with increasing difference in color. *With constant color, it may be shown, as before, that the optical center of gravity of the source of light depends simply and alone on the relative distribution of intensity in the spectrum of the source of light, as long as the absorption of the active substance is relatively the same for all wave-lengths in the light in question. We have then this important result, that under the* *assumed conditions, a definite optical center of gravity corresponds to any given source of light, which is the same for all Lippich instruments.* Of course, other sources of light which show the same relative brightness in their spectra, have the same optical center of gravity. If the light is purified by passing through light filters, the real source of light must now be taken as that corresponding to the new optical center of gravity. In what follows the optical center of gravity will be given for the sources of light mentioned, as far as this is possible with the present meagre and inaccurate determinations

We shall consider first the most commonly used homogeneous light, the sodium light. Every source of sodium light gives a continuous spectrum, in which, however, the light of the sodium lines is enormously in excess. If now, smaller rotations are measured with the unpurified sodium light, the rather dark field of view will disclose no color. But as soon as large angles of rotation are to be measured the field of view appears distinctly colored and the sodium light must be purified from foreign rays The color of the field depends on the rotation dispersion of the active substance. As the analyzer is always so placed that the yellow sodium light is nearly extinguished, it follows that with large rotations the blue rays, for example, which are much more strongly rotated than the yellow, are able to pass through the analyzer but little weakened and, therefore, impart a blue color to the field of view The shade depends on the rotation dispersion of the active substance, and the amount of the angle of rotation. In the course of time a large number of absorbing substances have been suggested to purify the sodium light,[1] of which, up to the present, the Lippich sodium light filter is the best, if for the moment we leave the complete spectral purification out of consideration; therefore this Lippich light filter only will be specially described.

The Lippich sodium light filter is an absorption cell consisting of two chambers which the light passes in succession, and which are closed by plane plates.[2] The larger of the two chambers has a length of 10 cm., the smaller a length of 1.5 cm. The large chamber is filled with a filtered 6 per cent. solution of potassium dichromate, in water In the smaller cell there is a solution of uranous sulphate, US_2O_8 This is deep green and must be made by reduction of the corresponding uranyl salt, USO_6. As the uranous salt solution passes into the other by oxidation in the air, a perfectly air-tight cell must be provided, and the solution must be renewed from time to time. The uranous sulphate solution is made as follows · 5 grams of pure uranic sulphate is dissolved in 100 cc of water and 2 grams of pure zinc in powdered form added. Then 3 cc. of concentrated sulphuric acid is added in three portions, waiting after each addition until the reaction is nearly complete ; the flask must remain closed After the addition of the last portion of acid the closed flask is allowed to stand about six hours ; the liquid is then filtered and filled into the chamber in such a manner as to leave the smallest possible air bubble After a day the solution comes to rest and remains one or two months constant. The weights and volumes given above must be adhered to within $^1/_{100}$ of their amounts While the potassium dichromate absorbs a part of the green rays and the blue rays, the uranous sulphate solution has a wide and deep absorption band in the red which reaches nearly to the D lines. A spectrum is, therefore, obtained in which only a small band with the D lines in the middle is present. The two solutions produce so complete a purification of the sodium light that even with a rotation of 50° and a strong illumination, difference in color is scarcely perceptible It is, therefore, desirable that chemists in general should employ this Lippich filter for the purification of sodium light, and especially for the reason that thereby the results of different observers would be comparable among themselves

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[1] The light filters must be placed between the lamp and the illumination lens

[2] It is made by Schmidt and Haensch, Berlin.

148. **Optical Center of Gravity of Sodium Light.**—Completely purified sodium light consists of the light of the two D lines and extremely little light of adjoining wave-lengths. Following Bell[1] we shall take the wave-length of the less refrangible sodium line D_1, as 589.62 $\mu\mu$, and of the more strongly refrangible one D_2, as 589.02 $\mu\mu$. In close agreement the observations of Soret and Sarasin,[2] and of Lippich[3] have shown that

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[1] Bell Phil Mag [5] **25**, 245, 350 (1888).

[2] Soret and Sarasin Compt. rend, **95**, 635 (1882)

[3] Lippich Wiener Sitzungsber, II, **99**, 722 (1890)

for a quartz plate 1 mm. in thickness the difference in rotation of the two D lines corresponding to the 0.60 $\mu\mu$ is about 160″ [1] Therefore a difference in rotation for 1 mm. of quartz, $\varDelta\beta$, corresponding to a change, $\varDelta\lambda$, in the wave-length in the neighborhood of the D lines may be calculated from the equation, $\varDelta\beta/\varDelta\lambda = -266\left[\frac{\angle\, sec}{\mu\mu}\right]$. If, therefore, we determine as Lippich did, the rotation β of a quartz plate for homogeneous light of wave-length $\lambda = D_2$, for example, and then the rotation β_1, for any other sodium light, we are able in the simplest manner, by aid of the above equation, to calculate the optical center of gravity corresponding to β_1. But this optical center of gravity is not peculiar to the quartz alone, but it holds good for all substances, since, as was explained in the last paragraph, the optical center of gravity of a source of light is independent of the rotation dispersion and of the size of the angle of rotation. It is, therefore, possible to find, with the aid of a quartz plate, the optical center of gravity of the different kinds of sodium light.

We may now calculate this optical center of gravity for perfectly purified sodium light, and it may be assumed that it contains only the light of the two D lines. According to Dietrich[2] the relation of the intensities of the two lines is $D_2/D_1 = 1.6$. By aid of this value and the wave-lengths given above for the D lines the optical center of gravity of the fully purified sodium light is found to be 589.25 $\mu\mu$, the method of calculation need not be discussed here. Lippich has experimentally determined the optical center of gravity for several sodium lights;[3] the wave-lengths of the center given in the table below differ from those stated by Lippich in the paper cited, by a constant difference, because he assumes a wave-length for D_2 different from that we have taken above. Finally, it is possible to calculate from some observations of Landolt[4] the optical center of gravity of unpurified sodium light (Landolt sodium lamp with NaCl) as 588.06 $\mu\mu$. In the following table the determined optical centers are grouped for comparison.

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[1] About the same value is given by the Boltzmann dispersion formula for quartz.

[2] Dietrich: Wied. Ann., **12**, 519 (1881).

[3] Lippich: Ztschr. für Instrum., **12**, 333 (1892).

[4] Landolt: Ber. d. chem. Ges., **27**, 2885 (1894).

OPTICAL CENTERS OF GRAVITY OF SODIUM LIGHT, ASSUMING 589.02 $\mu\mu$ AS THE WAVE-LENGTH OF D_2.

No.	Source of Light	Purification	Wave-lengths in $\mu\mu$
1	Bunsen burner with NaBr	Layer of a 9 per cent aqueous solution of $K_2Cr_2O_7$ 10 cm thick	592.04
2	Bunsen burner with NaCl	Layer of a 9 per cent aqueous solution of $K_2Cr_2O_7$ 10 cm thick	589.48
3	Bunsen burner with NaCl or NaBr	Lippich's sodium light filter, $K_2Cr_2O_7$ and US_2O_8	589.32[1]
4	Sodium light	Perfectly purified spectrum light The two D lines only	589.25
5	Landolt's sodium lamp with NaCl	Layer of a 6 per cent aqueous solution of $K_2Cr_2O_7$ 1.5 cm thick	588.94
6	Bunsen burner with NaCl	Layer of a 9 per cent aqueous solution of $K_2Cr_2O_7$ 10 cm. thick, and layer of a 13.6 per cent aqueous solution of $CuCl_2$ 1 cm thick[2]	588.91
7	Landolt's sodium lamp with NaCl	Not purified	588.06

It must be again remarked that these optical centers of gravity are exact only when the active substances under investigation do not appreciably alter the distribution of the intensity of the light from the source employed. If, in illustration, the rotation of a quartz plate is found to be 20° with light No. 1, the same plate will show a rotation of 20.27° with light No. 7; the difference amounts to 16.2 minutes of arc, certainly a considerable amount. It is plain, therefore, how important it is in statements of rotations for sodium light to give at the same time the optical center of gravity of the light used, as otherwise the rotations are uncertain to the extent of 1 per cent. or more. If we consider, for example, the results which the different observers found in the determination of the Verdet constant for the electromagnetic rotation of the plane of polarization, it is evident that the measurements of these different observers are not directly comparable with each other.[1] Nearly every one of the seven observers employed a different source of sodium light and method of purification, and besides this, several values have even been found with the Laurent half-shadow instrument (see §113); furthermore, the electromagnetic rotation dispersion for carbon disulphide and water is somewhat greater than the natural rotation dispersion of quartz

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[1] The optical center of gravity is therefore found midway between the two D lines and it is further seen that, after purification with the Lippich filter, even large variations in the intensity of the sodium light do not appreciably affect the optical center of gravity.

[2] One gram of cupric chloride to 6.35 cc. of water.

149. **Spectral Purification of Sodium Light.**[2]—In very exact work physicists will always prefer spectral purification of light to that by means of filters The spectral purification has always this great advantage over the filter method, that it permits the yellow rays to pass undiminished into the instruments while in the light filters, a certain amount of the light is always absorbed For the purpose of spectral purification, it is not recommended to use the Wernicke liquid prism, because, in consequence of the heating effect, the course of the rays is subject to constant changes; it is much better to use glass prisms. The following method of spectral purification of sodium light has been found by the author through long ex-

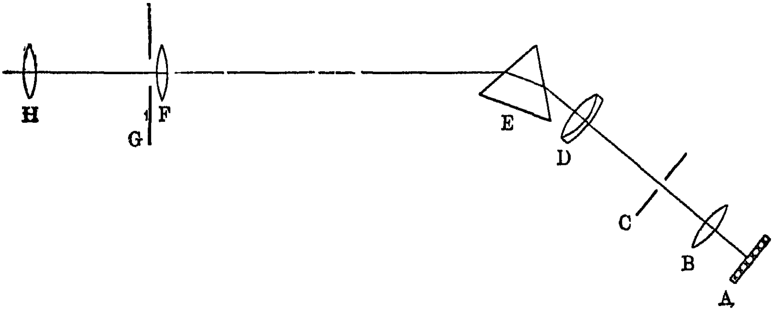

Fig 68

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[1] A tabular compilation of all the absolute determinations is found in Ztschr fur Instrum, 16, 283 (1896) Notice, especially, the almost impossible accuracy with which several observers claim to have established the value

[2] See, also, Brodhun and Schönrock Ztschr für Instrum, 16, 244 (1896)

perience to work well ; it may be used also in the purification of any other homogeneous light. By aid of the lens B (Fig. 68), a sharp image of the source of light A is thrown on the slit-screen C. The light which passes through the slit falls on the achromatic lens D and is then decomposed by the flint glass prism E, placed in position of minimum deviation. A sharp image of the luminous slit C, with the spectrum, is thrown on the second slit-screen G by the lens D. In order to secure the greatest possible dispersion, the distance between D and G is taken rather great, say 2 to 3 meters. The rays are then sufficiently parallel in passing the prism E. Just in front of the slit G there is a lens F, which produces a sharp image of the lens D on the illuminating lens H of the Lippich apparatus. The slit G, which passes the purified sodium light, must naturally have such a position with reference to the lens H that the latter will produce a clear image of G at the analyzer diaphragm. As D is pictured at H, it follows that the former must be uniformly illuminated by the slit C, which however may be accomplished without difficulty. Aside from reflexions, there is, therefore, no loss of light on the way from C to H. The active sections of the lens D and prism E must be chosen large enough, so that the polarizer diaphragm will be quite filled with light. The width of the slit G is, of course, made only as great as required by the analyzer diaphragm and focal length of the illumination lens H in order to secure maximum brightness in the field of view ; and, accordingly, the slit C is made so narrow that its enlarged image formed by the sodium rays is just sufficient to fill the slit G. As regards the centering of the course of the rays, it may be remarked that we begin with H and place G, then F, and the following pieces in position. Of course, the pieces from B to G need not be united in one apparatus ; it is better to have them attached to small stands which may be moved into the right positions and then made fast to the table with wax. Although the light rays, if the dispersion is sufficiently great, must pass through a distance of 5 or 6 meters from the source of light to the eye of the observer, it is still possible to build up the whole apparatus in a rather small room if a plane mirror is placed in the prolongation of the axis of the apparatus between E and F. The pieces from A to E can then be built up parallel to the apparatus and but slightly removed from it, and the sodium light thrown into the instrument by aid of the mirror. The spectral purification of the light secured by this method is so perfect that even with an angle of rotation of 500°, the slightest color in the field of view is not apparent.

150. **Dependence of the Optical Center of Gravity on the Brightness; that is, on the Amount of Luminous Vapor in the Unit of Volume of the Source of Light.**—We have now to consider the question: Is the optical center of gravity of a purified homogeneous light a function of the brightness of the light? Although the case of sodium light is somewhat complicated, we shall take it up first, since this homogeneous light is the one most commonly used. We shall assume then, in what follows, completely purified sodium light; that is, light consisting of the two D lines and extremely little of neighboring wave-lengths, such as is obtained by the method of spectral purification described in the last paragraph. The relative distribution of brightness in the spectrum of this sodium light corresponds approximately to Fig 69 in which, as abscissas, the wave-lengths λ are expressed in $\mu\mu$, while the ordinates represent the intensities for the corresponding wave-lengths[1] The light of the line D_2 is, according to Dietrich, about 1.6 times as bright as that of D_1. After satisfactory spectral purification light be-

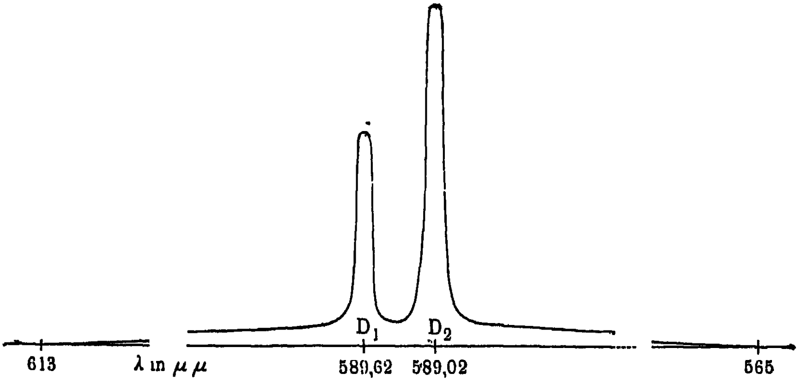

Fig 69

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[1] The false light is, of course, much too bright in the representation.

tween the wave-lengths 613 $\mu\mu$ and 565 $\mu\mu$, approximately, will enter the polarization apparatus; as this spectrum is very long for the dimensions chosen in the figure, only the middle and end portions are represented. *The optical center of gravity of purified sodium light from all sources is the same as long as the mean wave-lengths of the two D lines, and also their relations as regards brightness, are constant.*[1]

We may consider first, a source of sodium light of constant luminosity, which, after purification, reaches the illumination lens of the instrument with a perfectly definite optical center of gravity, and ask now if this center is altered if the light at any part of its path is uniformly weakened. This could be the case, only if the wave-lengths were variable with the intensity. Now, Lippich[2] has shown experimentally the constancy of wave-length with different values of the intensity to within $^1/_{100\,000\,000}$ of the value of the wave-length. His conclusions were later confirmed by Ebert,[3] who obtained results by the method of high interferences which, with proper homogeneous light, showed constancy in wave-lengths to within $^1/_{1,000,000}$ for values of the intensity varying between the limits of 1 and 250 Ebert was able to show for the light of the two D lines especially, that a diminution to 3 per cent. of the original brightness did not change the mean wave-lengths $^1/_{500\,000}$ of their value, that is, not by 0 001 $\mu\mu$ *We have then this important result, that with unchanged emission from the source of light, the optical center of gravity does not vary with the intensity.*

Now let us suppose the emission from the source of sodium light to change by altering, for example, the brightness As far back as 1871, Zollner[4] showed that when by moving the salt globule more or less completely into the Bunsen flame, different amounts of sodium vapor were produced, the line D_2 increased in width more rapidly than D_1 with increasing brightness, and that D_1 widened more rapidly toward the side of greater wave-lengths than toward the other, while no such displacement of the center of D_2 on widening was to be observed. From these observations, it follows that a change in the optical center of gravity is indeed possible with a change in brightness in the sodium light. On what does the widening of a spectrum line depend? As even the most homogeneous spectrum line is formed by a series of elementary rays whose wave-lengths are infinitely close together, it must follow that the intensities of the elementary rays are a continuous function of the wave-lengths. The brightness of the spectrum lines cannot, therefore, change suddenly on the sides but must gradually decrease to zero. If such a line is broadened, it is the intensities of just those wave-lengths on the edges of the spectral lines which are so much increased that they become perceptible to the eye. We must, of course, distinguish between this broadening and the displacement of the mean wave-length (the optical center of gravity) of the spectrum line in question; this displacement may depend on a broadening of the line as well as on a change in the form of its intensity curve.

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[1] The continuous spectrum of the false light in the sodium light does not change the optical center of gravity of the two D lines, because the brightness of the whole range of the narrow portion of the spectrum from which light enters the apparatus may be taken as constant.

[2] Lippich. Wiener Sitzungsber, II **72**, 355 (1875)

[3] Ebert Wied Ann, **32**, 337 (1887)

[4] Zollner Pogg Ann, **142**, 88 (1871)

The observations of Zollner were fully confirmed by work of Ebert[1] As the latter, in these investigations, made quantitative measurements by the method of high interferences of the changes in mean wave-lengths of several lines of the spectrum, so that we have full data concerning the amount of possible displacements, this work of Ebert's must be regarded as of great importance in polarimetry and will, therefore, receive here closer attention. In his experiments, Ebert employed a Terquem burner, and modified the emission of light by moving the salt globule to a greater or less depth in the flame. As long as the salt just touches the edge of the flame, the vaporization and brightness are small, but these increase as the globule is pushed further into the flame until a point is reached near the inner cooler zone where the vaporization again decreases. With such alterations in brightness, Ebert found displacements of the mean wave-length of sodium light amounting to 0.044 $\mu\mu$, and increasing toward the less refrangible end of the spectrum, with increase in brightness. *At the same time Ebert showed for sodium light as well as for several other spectral lines, that primarily neither the thickness of*

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[1] Ebert Wied Ann., 34, 39 (1888)

the luminous layer nor the temperature of the source of light or the chemical changes taking place in it cause any changes in the wave-length, but that the mean wave-length depends simply and alone on the density of the vapor; that is, on the amount of vapor of the luminous substance in the unit of volume, and varies with alterations in the density of this vapor. It is also true that the amount of change for the different sodium salts under the same conditions of vaporization is, in general, not the same; but the variations are not large. If now a change in brightness obtained by aid of a Terquem burner and salt bead produces a displacement of the optical center of gravity of sodium light amounting to 0.044 $\mu\mu$, one may not be mistaken in assuming that with much greater changes in illumination the displacement of the center will probably be still more marked. This view has recently been completely verified by Schönrock,[1] and by aid of polarization apparatus which for such investigations is doubtless more sensitive than Ebert's method of high interferences.

Schönrock worked with a Lippich half-shadow instrument, and employed as source of light the Linnemann oxygen blast-lamp described in §142, in which sticks of fused sodium carbonate were vaporized, the sodium light obtained was purified perfectly by a flint glass prism with a ray path of about 3 meters It could then be shown easily that the optical center of gravity varied considerably with the brightness of the flame, since the amount of an angle of rotation must vary correspondingly If by use of a perfect quartz-plate or a cane-sugar solution an angle of rotation of about 100° is obtained, this is found to decrease about 140 seconds of arc when the stick of sodium carbonate is moved more and more into the hottest part of the flame. The zero point of the instrument is in no wise changed in the operations Therefore, according to the formula developed in §148,

$$\varDelta\beta/\varDelta\lambda = -266\left[\frac{\angle\, sec}{\mu\mu}\right],\ \beta = 21\ 7^\circ$$

the optical center of gravity of sodium light must be moved about 0.11 $\mu\mu$ with increasing brightness, that is, about one-fifth of the distance between the two D lines and toward the red end of the spectrum. This displacement is in the same direction as shown by Ebert, but in consequence of the much greater variation in brightness is more than twice as large as he found Without doubt by working with the du Bois soda pencils described in §146 still greater displacements of the optical center could be demonstrated. At the same time Schönrock found in complete agreement with the results of Lippich and Ebert, by aid of a Nicol prism placed in front of the illumination lens of the instrument, that with constant emission from the source of light the wave-length of the optical center of gravity does not change with the intensity of the light. The displacement of the center for sodium light is doubtless due not only to the unsymmetrical widening of the line D_1, but also to a change in the relation of the lines D_1 and D_2 to each other as regards brightness. But this point remains to be cleared up by future work. In §148 the optical center of gravity of perfectly purified sodium light is calculated as 589 25 $\mu\mu$; we know now that this value is probably correct for a certain mean brightness of the sodium light, but that in addition it may vary by 0 11 $\mu\mu$ by changes in the emission from the source of light

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[1] Schönrock "Die Thätigkeit der Physikalisch-technischen Reichsanstalt," Ztschr. fur Instrum 17 (1897)

As with sodium light the optical centers for all other lines or perfectly purified homogeneous lights change more or less strongly with variations in the amount of vapor in the unit volume of the source of light. In his work referred to above Ebert made quantitative measurements of the displacement for some lines of thallium, lithium, potassium, and strontium Without exception he found that the widening of the lines was stronger toward the end of less refrangibility than toward the other, so that with increasing brightness the optical centers of gravity moved toward the red end of the spectrum The displacements observed by him are given in the following short table, for which it must be remembered that the changes of brightness were produced by aid of a salt bead and Terquem burner only.

DISPLACEMENT OF THE OPTICAL CENTERS OF GRAVITY OF SOME SPECTRUM LINES, ACCORDING TO EBERT.

Source of light	Wave-lengths in $\mu\mu$	Displacement in $\mu\mu$
LiCl, Li_2CO_3	670 8	0 06
TlCl	535 1	0 026
KCl	768 0	0 046
KCl	404 6	.. [1]
$SrCl_2$	460 8	0 019

In their paper "Ueber die Spectren der Alkalien," Kayser and Runge make the following statement :[2] "The majority of the lines of the alkalies are not, however, sharply defined, they broaden by increase in the amount of vapor, and either toward both sides or, more commonly, toward the red end of the spectrum, occasionally however, toward the violet end only. Such broadened lines often reach a width of two to three $\mu\mu$" The general conclusion is therefore warranted that the optical center of gravity of a spectrum line is not a constant but is a function of the emission from the source of light. Since the Arons mercury light, to be described later, has recently been made available for polarimetric measurements, it may be in order to discuss briefly the spectrum lines of mercury. It is well known that the different spectra of one and the same chemical element show variations depending on whether they are flame, spark, or arc light spectra. In the case of mercury these differences are very large,[3] so that the strongest lines in one spectrum may be in part wholly wanting in the other. It would appear probable, therefore, that the lines of mercury must change strongly with changes in the light arc, which in turn changes with the intensity of the producing current; Ebert states that the bright green mercury line, 546 $\mu\mu$, increases on one side only, which, in all probability, would have a displacement of its optical center of gravity as a consequence. What conclusion must be drawn now for polarimetry from this variability of the optical center of gravity of purified homogeneous light?

[1] A displacement was found but not measured

[2] Kayser and Runge Wied Ann , 41, 302 (1890)

[3] Kayser and Runge *Ibid*, 43, 385 (1891)

In the first place in all polarimetric measurements, whether of absolute amounts of rotation, or of differences of rotations, the emission from the source of light must be kept constant, and this may be reached in a satisfactory manner even in investigations of length. *In the second place it is necessary that along with the rotations the optical center of gravity of the light used must be determined and defined with corresponding accuracy, as otherwise the measurements of different observers are not comparable with each other.* It is not sufficient to merely state that one has used sodium light after perfect spectral purification, as even then its optical center of gravity remains uncertain to about 0.1 $\mu\mu$. This uncertainty corresponds to a difference in rotation of 25″ in an angle amounting to 20°, such an angle may often be measured without difficulty to within 8″. If then the expected accuracy of the method is not to be illusory the wave-length of the corresponding optical center of gravity must be given to within 0 03 $\mu\mu$. *From this it is seen that in general an angle of rotation may be found with a good polariscope with a degree of accuracy which is much greater than the accuracy with which the corresponding optical centers of gravity may be measured and expressed* Whether it will ever be possible to carry the determination of the optical centers of homogeneous lights so far that they will correspond in accuracy to the delicacy of the modern polarimetric apparatus, remains for the future to show.[1]

151. **Absolute Determination of the Rotation of Sodium Light for Quartz.**—As we have now seen the several variations to which the optical center of gravity of sodium light from different sources is subject, we shall next attempt a review of the work done on the absolute rotation of quartz for sodium light, as already explained in §44, taking these disturbing variations into consideration. Passing over the oldest and very inaccurate measurements we come at once to the work of v. Lang A value is often quoted from work of v Lang done in 1875[2]

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[1] This will be possible as soon as the rotation dispersion of quartz is sufficiently well established. Such an accurate determination of the rotation dispersion of quartz may be made, as is sufficiently clear from what has been said, only by aid of the Fraunhofer lines, and after improvements in methods discussed in the chapter on "Determination of Rotation Dispersion"

[2] v Lang · Wiener Sitzungsber., II, 71, 707 (1875).

which is misleading; in this work v. Lang investigated the dependence of the circular polarization of quartz on the temperature, but did not determine, as he himself explains, the absolute value of the angle of rotation, assuming the rotating power per millimeter as known. But in a second investigation he made an absolute determination.[1] By the aid of the Broch method to be described later, with sunlight, and using a double prism of right and left quartz about 33 mm. thick, he found at 20° C. a rotation of 21.724° per millimeter for the line D. We must take then as the optical center of gravity the mean between the two D lines, that is, 589.3 $\mu\mu$.

In 1878 Joubert[2] made absolute rotation determinations; but as he worked with the Laurent instrument and sodium light, the optical center of gravity being quite indefinite, his results do not call for consideration.

Following the Broch method with sunlight, Soret and Sarasin[3] determined the rotation of two quartz plates, about 30 and 60 mm. in thickness, for each of the two D lines. For the middle of the two lines (589.3 $\mu\mu$) we find as the mean value from these figures 21.708° per millimeter, for 20° C.

Soret and Guye[4] have made determinations with the same plate about 60 mm. thick, used by Soret and Sarasin. As they worked with a Cornu instrument (§110) and sodium bromide light, purified through the spectrum, the wave-length of the optical center may be taken as before, as 589.3 $\mu\mu$. The value of 21.723° per millimeter at 20° C. may be calculated as the mean value from their experiments.

More recently absolute rotation determinations have been made by Gumlich.[5] The optical center may be again taken as 589.3 $\mu\mu$, as he worked with the Lippich instrument and spectrum sodium light. He found, with four quartz plates of approximately 5, 6, 8, and 10 mm. thickness, values which varied between 21.717° and 21.731° per millimeter at 20° C. The mean value was 21.724°.

Finally, the author is in a position to give his own results for the absolute rotation of quartz. He (Schönrock) made his determinations with a perfect quartz plate, about 5 mm. thick, by aid of a Lippich instrument and sodium light which was absolutely purified through the spectrum, so that the optical center may be taken as 589.3 $\mu\mu$. From many measurements made at different times the value 21.722° per millimeter at 20° C., and accurate to ± 0.003°, is calculated, corresponding to the true optical center of gravity of the sodium light used; but this latter has not yet been found with a satisfactory degree of accuracy.

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[1] v. Lang. Wiener Sitzungsber., II, **74**, 209 (1876).

[2] Joubert. Compt. rend., **87**, 497 (1878).

[3] Soret and Sarasin. *Ibid.*, **95**, 635 (1882).

[4] Soret and Guye: *Ibid.*, **115**, 1295 (1892).

[5] Gumlich. Ztschr. fur Instrum., **16**, 97 (1896).

As, therefore, all these observers have made their determinations very nearly for the same center, 589.3 $\mu\mu$, their measurements must be comparable with each other. The results are given in the following short table:

Observer	Rotation of quartz per millimeter at 20° C.
v. Lang	21.724°
Soret and Sarasin	21.708
Soret and Guye	21.723
Gumlich	21.724
Schönrock	21.722

With exception of the value of Soret and Sarasin the agreement is quite a remarkable one. *It may be said with certainty that, using perfectly pure spectrum sodium light, 1 mm. of quartz, with a certain mean brightness of the light, will rotate the plane of polarization exactly 21.723° at a temperature of 20° C.* But on account of the variation in the optical center of gravity with the brightness of the source of light the rotation may vary by about ±0.004° per millimeter. *There may accordingly be some reason for a redetermination of the absolute rotation of quartz only when the corresponding optical center is found with an equal degree of accuracy.*

152. Relation of the Angles of Rotation, α, and α_D.—In addition to the illumination of saccharimeters a white light is employed in the determination of the angle of rotation, α_j, for mean yellow rays by aid of the Robiquet polariscope (§ 100). As seen by the expression itself, "mean yellow rays," the angle of rotation, α_j, is not accurately defined; the wave-length corresponding to it may be taken as about 556 $\mu\mu$.[1] The rotation referred to this, following Biot's suggestion, is represented by α_j (*jaune moyen*).

As the wave-length of mean yellow light is less than that of D (589 $\mu\mu$) the values for α_j are always much larger than those for α_D. For quartz, as an illustration, we have per millimeter, $\alpha_D = 21.72°$ and $\alpha_j = 24.5°$; these formulas for conversion are therefore used:

$$\alpha_j = \frac{24.5}{21.72}\alpha_D = 1.128\alpha_D, \text{ and } \alpha_D = \frac{21.72}{24.5}\alpha_j = 0.887\,\alpha_j.$$

But on account of unequal rotation dispersion for different substances the relation of α_D to α_j is a variable one. The deviations from the above values may amount to 10 per cent. or more.

As the rotation α_j does not correspond to any accurately definable ray, the determination of α_j is not satisfactory and at the present time is scarcely made It must be pointed out here that when a rotation is measured in a half-shadow apparatus with white light the angle obtained is not accurately α_j; see §153.

There are in the literature a large number of observations made by Biot[2] with red light obtained by aid of glass colored with cuprous oxide, and corresponding approximately in refrangibility to the Fraunhofer line C (656 $\mu\mu$) From the statement that this light is rotated 18 41° by 1 mm. of quartz its wave-length is calculated as about 637 $\mu\mu$. For quartz, therefore, the rotation of this red light is related to that for D as 1 to 1.18

153. **Optical Center of Gravity of White Light.** — The chemist is sometimes in the position where, instead of using yellow light, he is obliged to employ white light We shall therefore consider the optical center of gravity of white light more closely, *under the assumption that the rotations are measured with a Lippich half-shadow instrument.* An optical center of white light can not be directly defined, as it is subject to considerable variations according to the source of light employed. Sunlight, gas light, petroleum light, Welsbach light, electric light, zir-

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[1] Landolt Sitzungsber der. Akad. Berlin, 1896, p 790

[2] Biot. Mém. de l'Acad, 3, 177 (1820)

cona light, lime light, and so on, have all a different distribution of brightness in the spectrum and, therefore, according to §147, different optical centers of gravity. *With white light illumination, however, only very small angles, at most 3°, may be measured, because with larger rotations, the field of view shows considerable color variations. And, above all, the investigated substances must be colorless and as clear as water.* If the active substance is colored, it will have an absorption spectrum, and will, therefore, alter more or less strongly the composition of the white light; the white light will, at the same time, be filtered by the colored body, and in this way the relative brightness of different parts of the spectrum of the original light will be totally altered. For one and the same source of white light the optical center varies, therefore, from substance to substance, if they are colored.[1] That these changes in the optical center are very considerable is shown by the observations of Holzer,[2] the results of which could be predicted from what has been said In the investigation of colored substances, therefore, even when the color is slight, the use of white light must be given up and an intense sodium light provided.

The following experiments were made to find the optical center of one white light, the Welsbach light, with some degree of accuracy. The small angles of rotation were secured by combination of positive and negative quartz-plates, a positive plate about 1 49 mm. thick and a negative plate about 1.46 mm. thick, gave together a rotation of about + 0 6°, while the same negative plate with a positive plate about 1.6 mm thick gave a positive rotation of about 2 9°. These two angles of rotation were measured in the Landolt apparatus (§117) with the following three sources of illumination · First, with sodium light made by the Landolt sodium lamp and purified by the Lippich sodium light filter, then with the Welsbach light filtered through a layer of 6 per cent. potassium dichromate solution 1.5 cm. thick, and finally with pure Welsbach light. In using the last sources of light, the field of view was colored, especially in measuring the larger angle of rotation;

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[1] The Landolt ray filters depend on this.

[2] Hölzer · Ber d chem Ges, **15**, 1932 (1882).

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notwithstanding this, the adjustment was always made to secure uniform shade as nearly as possible, the error of adjustment being in the mean about ± 1.5 minutes of arc, with a half-shadow of 3°. Any effects of temperature changes may be eliminated in such long experiments by regularly changing the sources of light and employing them, for example, in this order, I, II, III, I, III, II, I, so that the mean values for each source of light correspond to one and the same mean temperature. The results obtained are given in the following table.[1]

By quartz-plates	Sodium light purified by the Lippich filter	Welsbach light through layer of 6 per cent solution of $K_2Cr_2O_7$ 1.5 cm. thick	Simple Welsbach light
Angle of rotation 1	0.60°	0.61°	0.68°
Angle of rotation 2	2.95°	2.94°	3.39°
Optical center in $\mu\mu$ ...	589.3	589	551

To within about ± 0.01°, the same angles are found with the pure sodium light and the filtered Welsbach light, so that the optical center of the latter may be taken also at 589 $\mu\mu$. On the other hand, the results found with the simple Welsbach light, α_w, are much larger than the corresponding α_D. If we recall now that the rotation of quartz for pure sodium light is 21.72°, we may calculate by aid of the known dispersion formulas for quartz that the optical center of gravity of the Welsbach light is about 551 $\mu\mu$. We have then the conversion formulas

$$\alpha_w = 1.149\alpha_D \text{ and } \alpha_D = 0.870\alpha_w.$$

But as the relation of α_D to α_w varies in different substances because of unequal rotation dispersions, it must always be remembered that for other bodies than quartz, the values of α_D calculated by the above factor from observations of α_w may be in error to the extent of 10 per cent or more. It is, therefore, recommended not to use the simple Welsbach light at all, but when necessary, to employ this light purified by the potassium dichromate solution as above defined, since in this case a reduction is not required.

If one is obliged to measure angles of more than 3° with white light, this should not be done under any circumstances with a half-shadow instrument with circular graduation, but the rotation may be found with a *half-shadow saccharimeter*, with which, using the double wedge-compensation, angles of ± 34° may be measured. The conditions here are very much more favorable, because the rotation dispersion is very largely compensated by the action of the compensating quartz-plate in the wedge, so that its influence on the measured angle of rotation is small; colored substances also, may therefore be investigated in saccharimeters. If then the rotation in Ventzke degrees be multiplied by the factor 0.347, as given in §127, it may be at least said that the product obtained gives the angle of rotation in circular degrees for sodium light with an error of 2 to 3 per cent. at most.[1] But there is no object in trying to find a more accurate reduction factor for each individual substance, because, on account of rotation dispersion, temperature effects, and variations in rotation with the kind of illumination and color sense of the observer, it is never possible to make accurate determinations, free from appreciable systematic errors, in a saccharimeter. Whenever possible, therefore, avoid the use of a saccharimeter and secure for illumination of a polariscope the most intense sodium light available, the production of which may be, moreover, accomplished without great difficulty.

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[1] Without doubt, other results would be obtained by a color-blind eye.

d. Determination of Rotation Dispersion

154. Method of Broch. To find the rotation dispersion of a substance, it is necessary to determine the angles of rotation for light of different wave lengths. This may be done by aid of one of the polarization instruments described, using different kinds of homogeneous light, which method will be later explained. But first, several other methods must be considered. A procedure which permits the determination for a whole series of rays of known wave-lengths was given by Broch,[2] and simultaneously by Fizeau and Foucault.[3] In this process, illumination is furnished by sunlight which, by aid of a heliostat, is thrown horizontally into a darkened room. The rays pass in the following order: the vertical slit A (Fig. 70), the polarizer B, the analyzer C, the prism D placed in position of minimum deviation, and the telescope E F which must be provided with cross hairs. In order to adjust the apparatus, the principal section of the movable analyzer C is placed parallel to the principal section of the polarizer B, the slit A is illuminated with sodium light and the ocular F of the telescope is focused sharply on the image of the slit A formed by the achromatic objective E. On removing the sodium light and admitting sunlight, a pure spectrum with the Fraunhofer lines is seen with the ocular F In order to bring any desired part of the spectrum into the center of the field of view, the telescope must be movable horizontally around a fixed axis passing through the center of the prism First, the analyzer C is placed in the position of greatest darkness, without an active substance following, this is the zero point. Then when the active body is placed between C and B, the spectrum with the Fraunhofer lines appears again in the telescope If now the analyzer C is turned, a position is found at which a vertical dark band appears in the field of view and, with further rotation of C, moves across it, an essential condition for this, however, is that the rotation dispersion of the substance must be rather large as compared with the dispersion of the prism. The phenomenon of the dark bands depends on the fact, that in the rotation of the analyzer those rays are extinguished, one after the other, whose planes of polarization coincide with the principal section of the analyzer. If the cross hairs of the telescope are focused on one of the Fraunhofer lines at the start, and then, by movement of the analyzer, the dark band is brought to center with the cross hairs, the rotation read off on the circle shows the amount of rotation for the line in

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[1] This follows from the data of Landolt, Sitzungsber. der Akad., Berlin, p. 959 (1887).

[2] Broch, Dove's Repert. d. Phys., 7, 113 (1846).

[3] Fizeau and Foucault, Compt. rend., 21, 1155 (1845).

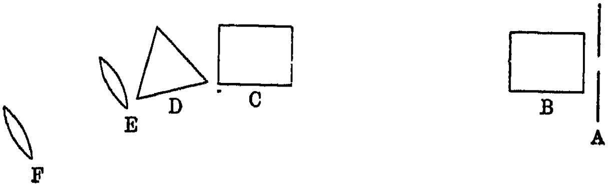

Fig 70

question. In this manner the rotation for each one of the Fraunhofer lines may be found. In place of cross hairs, it is preferable to employ parallel fibers. The dark band is narrower and sharper, the larger the angle of rotation, and consequently, the rotation dispersion. The Fraunhofer lines and the corresponding wave-lengths are given in the table below

Fraunhofer lines	Wave-lengths in $\mu\mu$.	Fraunhofer lines	Wave-lengths in $\mu\mu$
A	759 4	*b*	517.5
a	718 6	*F*	486.1
B	686.7	*G*	430 8
C	656 3	*h*	410 2
D	589 3	*H*	396.9
E	527 0		

Soret and Sarasin[1] in their determination of the rotation dispersion of quartz have avoided the rather inaccurate zero-point adjustment in this manner that they placed a negative quartz-plate, for example, in position first and brought the dark band into coincidence with a line of the spectrum, then, after removing this plate, a positive one was substituted and by movement of the analyzer the dark band was again brought into coincidence with the same line of the spectrum. From the rotation of the analyzer there is found, therefore, for the line in question, an angle which corresponds to that of a positive or negative quartz-plate, the thickness of which is equal to the combined thicknesses of the positive and negative plates used.

Through several improvements, Lippich[1] has made the Broch method a tolerably accurate one, but for the details, his original paper must be consulted

Finally, by use of a quartz double plate of variable thickness, G. Wiedemann[3] has essentially improved the Broch method. The double plate consists of two quartz wedges whose principal surfaces are ground vertically to the optical axis, and each one of which consists of an upper right-rotating and a lower left-rotating half. By aid of a micrometer screw one of these wedges may be moved in front of the other. The vertical slit A (Fig 70) is brought between B and C, and at a slight distance from B, and then between A and B, and immediately behind the slit, the double plate is so placed that its junction edges lie horizontally. The double plate must stand vertically to the direction of the light rays, so that they will pass through in the direction of the axis Using sunlight, the spectrum with the Fraunhofer lines is found as before in the telescope, these lines being broken into upper and lower halves by the horizontal juncture surface of the double plate. As the plane of polarization of each color is turned to the right by the upper plate, and through the same angle to the left by the lower plate, it follows that for any position of the analyzer the spectrum does not show the same colors above and below, but at any given time those are extinguished for which, above and below, the angles of rotation differ by some multiple of 180°. If then, the same color is to be extinguished above and below, the rotation for this color must be a multiple of 90°; in this case, the polarizer and analyzer must stand in crossed or parallel position. Just which color is extinguished depends on the thickness of the quartz double plate; if this thickness may be varied within sufficiently wide limits, it will be possible to follow the bands shut out from one end of the spectrum to the other and to bring them to coincide with any Fraunhofer lines desired. The determination of an angle of rotation for a Fraunhofer line is then made as follows · The line in question is brought between the parallel threads, the analyzer is then turned until at some point of the spectrum the two dark bands stand with one exactly above the other, and the movable wedge is then shoved until the dark band lies between the parallel threads; this gives the zero-point position of the analyzer. If the active substance is now placed between the analyzer and the slit, the bands no longer stand one above the other, but to secure this the analyzer must be turned through the same angle by which the line chosen is rotated by the active body. It is assumed that the temperature of the double plate does not appreciably change during the measurements. The spectropolarimeter constructed much later by v. Fleischl[1] is nothing but a bad copy of the Wiedemann apparatus, the variable double plate of which is replaced by a simple quartz double plate of constant thickness, with which the rotation for a single definite color only may be measured.

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[1] Soret and Sarasin: Compt rend, **95**, 635 (1882) Their method has been given above by the author in more practical form

[2] Lippich: Wiener Sitzungsber II, **85**, 307 (1882)

[3] G. Wiedemann. Lehre von der Elektricität, **3**, 914 (1883)

155. **The Method of v. Lang.**—The main drawback in the Broch method is that it depends on the not always available sunlight. But v. Lang has shown[2] that the Broch procedure may be easily so changed that instead of sunlight with the Fraunhofer lines ordinary white light with artificial spectral lines may be employed. The arrangement of the apparatus is preferably that shown in the illustration (Fig. 71) By aid of the lens B, a sharp image of the source of white light A is thrown on the slit C. The light passing the slit is led first through a simple Mitscherlich polariscope consisting of the illumination lens D, the polarizer E, and the analyzer F, which may be rotated, and then through an ordinary spectroscope G to L. The focal distance of the illumination lens D is equal to half the distance between D and G, and the slit C is so placed that a sharp image of it may be formed by D at the objective slit G of the spectroscope G is situated in the focus of the achromatic lens H, and the prism J in the position of minimum deviation The spectrum produced in the achromatic telescope K is seen at the ocular L along with two parallel vertical lines or fibers. The telescope K L is movable horizontally The adjustment of the spectroscope is accomplished in the usual well known manner. The following operations are necessary to determine the angle of rotation of a substance for a given spectrum line · 1. The zero point is found by turning the analyzer F to the position of greatest darkness 2. The white

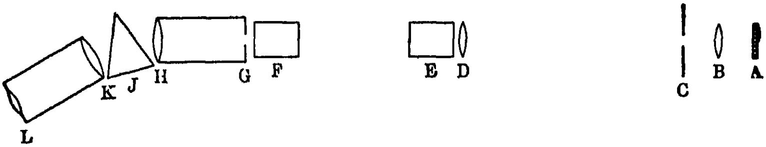

Fig 71

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[1] v. Fleischl. Repert d. Exper.-Phys., 21, 323 (1885), Wied. Ann Beibl, 9, 634 (1885)

[2] v. Lang Pogg. Ann., 156, 422 (1875)

light is shut off and between B and C, and near the slit the apparatus is placed which furnishes the lines of the homogeneous light in question, and the analyzer F is so turned as to transmit the largest possible amount of light. A continuous spectrum is no longer seen in the telescope, but only the sharp and bright spectrum lines. The telescope is then turned horizontally until the desired bright line comes between the parallel hairs The source of homogeneous light is then removed, the strong white light A admitted, the active substance placed in position and the analyzer F turned until a black band appears in the telescope. By further turning the analyzer, this band is brought exactly between the parallel hairs, and the analyzer graduation is then read off. By again admitting the line of the homogeneous light it may be determined whether or not the position of the telescope has suffered any change. If it is desired to work with the Wiedemann double quartz plate of variable thickness, described in the preceding paragraph, F must be placed between G and H, and the double plate directly in front of G and turned toward the polarizer E In regard to making the determinations of rotation the directions of the last paragraph obtain

In the production of the spectrum lines various sources of homogeneous light may be used Salts of metals may be introduced into the Bunsen flame by a platinum loop, and in particular the chlorides or carbonates of sodium, lithium, thallium, potassium, and strontium. The light of a Geissler hydrogen tube may be employed also If a little mercury or some bits of cadmium are introduced into a Geissler tube, the light emitted on warming these metals may be used. In the following table all these artificial lines are given with their wave-lengths, and as seen, they are sufficient for the determination of the rotation dispersion of a substance.

Color of the lines	Source of light	Wave-lengths in $\mu\mu$
Red	K α	768.0
	Li α	670.8
	H α	656.3
	Cd	643.8
Yellow	Na	589.3
	Hg	579.0
	Hg	576.9
	Hg	546.1
Green	Tl	535.1
	Cd 4	508.6
Blue	H β	486.1
	Cd 5	480.0
	Cd 6	467.8
	Sr δ	460.8
	Hg	435.9
	H γ	434.0
Violet	Hg	407.8
	K	404.6

156. Lippich's Method.—The methods of Broch and v. Lang give more accurate results the larger the rotation dispersion. But if this is small the dark band is broad and not sharp on the edges so that the adjustment is very inaccurate. In this case it is better to employ the method of Lippich[1] in the measurement of rotation dispersion. In this method the light passes into the spectroscope first and then into the polarization apparatus, which should be, preferably, the sensitive Lippich half-shadow instrument with double or triple field. The arrangement of the parts is shown in Fig. 72. By aid of the lens B a sharp image of the bright white light A is thrown on the vertical slit C of the spectrometer. C is situated at the focus of the achromatic lens D. The prism E is placed in the position of minimum deviation, and the light rays passing through it are thrown as a bright spectrum on the slit screen G, by means of the achromatic lens F, and in such a manner that only one color of the spectrum may pass through the slit and serve for the illumination of the polarization apparatus. The slit G, therefore, represents the source of homogeneous light, and must be given such a position that a sharp image of the slit may be formed by the illumination lens J, of the polarization instrument, on the analyzer diaphragm. In order to center the rays more completely it is recommended to add the lens H, immediately in front of G, which throws an image of D on the illumination lens J; but A and B must be then so centered that D appears uniformly illuminated. By turning the slit tube C D any desired part of the spectrum may be thrown into the polarization apparatus, but A and B must be attached in fixed position with reference to this tube; on account of its small dimensions and slight weight the Linnemann zircona light burner (§142) is recommended for this work If one employs sunlight a small movable mirror is attached in place of A, by aid of which, with the different positions of the slit tube, the heliostat light may be thrown directly into the tube According to Lippich the direct vision spectrometer of Hilger, in London, with the Christie half-prism[1] is also very satisfactory, as with this the simple turning of the prism is sufficient to bring any desired part of the spectrum to the slit G. The whole spectroscope, C to G, must first be graduated according to wave-lengths, in order to be able to give directly, for any position of C D, the mean wave-length of the light passing the slit G. For this purpose the slit C is illuminated

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[1] Lippich: Wiener Sitzungsber., II, 91, 1070 (1885).

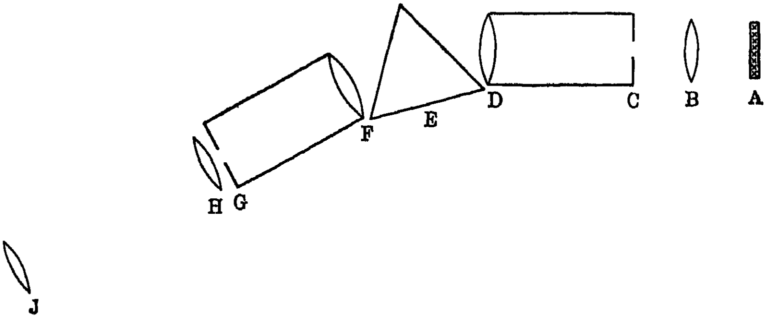

Fig 72

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[1] Proc Roy Soc, 26, 8 (1878), Pogg Ann Beibl, 1, 556 (1877).

with the several homogeneous lights described in the last paragraph, one after the other, and the tube C D is turned so that the image of the illuminated slit C coincides exactly with G, which may be easily verified by aid of a reading glass The different positions of the tube C D are read off on the graduated circle, and are tabulated along with the corresponding wave-lengths of the homogeneous light. In this way a large number of definite positions of the tube C D are determined for which accurately characterized homogeneous colors pass through the slit G, and the angles of rotation of these may then be measured with the polarimeter in the usual manner. In the graduation of the spectrum apparatus the Fraunhofer lines of sunlight may of course be used The greater the dispersion the smaller must be the slits C and G, in order that the light emerging from G may have the necessary homogeneity. If, finally, the rotation dispersion is very large, the Lippich method is then no longer applicable, since, in this case, a slit so narrow would be required that the necessary brightness of the field could not be secured; it is then better to apply the procedure of Broch or v Lang

Agreeing in principle with the Lippich method is that of Seyffart,[1] patented in 1886, for the determination of rotation dispersion But as the latter is very complicated as regards the optical as well as the mechanical construction, without, at the same time, reaching the accuracy of the Lippich method, it need not be discussed here at length. The spectrosaccharimeter introduced recently by Glan[2] resembles also the Lippich apparatus in principle, but is much inferior to it as regards convenience or accuracy in manipulation

157. **Lommel's Method.**—Lommel[3] has so modified the Broch method by addition of a quartz wedge that the final reading is made, as in the case of the Wild polaristrobometer (§103), on the disappearance of interference bands Sunlight is polarized by the prism A (Fig. 73), whose principal section makes an angle of 45° with the horizontal plane, and then reaches the vertical slit D. Just in front of this slit is a quartz wedge C,

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[1] Seyffart Wied Ann., 41, 113 (1890).

[2] Glan· *Ibid.*, 43, 441 (1891)

[3] Lommel · *Ibid.*, 36, 731 (1889)

with an angle of 7° or 8°, whose edge, parallel to the optical axis, is vertical with reference to the slit, and immediately following the latter is the analyzer E, the principal section of which either crosses or stands parallel with the principal section of the polarizer and, therefore, makes an angle of 45° with the horizontal plane. The refractive action of the wedge is corrected by that of a glass wedge, B, placed in reversed position The light leaving the analyzer is decomposed by the prism F, which is placed in the position of minimum deviation, and is then collected by the achromatic lens G to form a spectrum that may be observed by the ocular H. As readily , understood, this spectrum is filled with numerous dark, somewhat curved, interference bands which stand inclined with reference to the Fraunhofer lines, and it is also shaded by fine dark slanting lines. If the polarizer A is turned through 45°, the shading disappears through the whole spectrum (the zero-point). If now an active body is placed between A and B the bands appear again If, next, the polarizer be rotated, a position is found at which a vertical bright band, free from shade, enters the field of view and with further turning travels through the spectrum. By bringing this bright band to coincide with the various Fraunhofer lines, one after the other, so that each line bisects the band exactly, and the corresponding angle is then read off on the graduated circle of the polarizer, the angle of rotation of the particular Fraunhofer line is obtained The Lommel method may, of course, be so arranged that, as in v. Lang's method, artificial sources of light may be used.

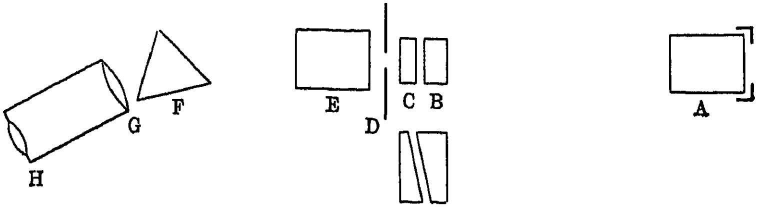

Fig 73

Reference only can be made here to Lommel's interesting determination of the rotation dispersion of quartz by aid of the interference phenomena on a quartz prism.[1]

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[1] Wied Ann, **36**, 733 (1889).

158. Landolt's Method with Use of Ray Filters.—While the methods thus far described for the measurement of rotation dispersion, necessitate the use of apparatus which is complicated for the chemist if not for the physicist, since the combination of a spectrometer with a polarimeter is always called for, that of Landolt[1] with ray filters requires the use of a polarimeter only. It may always be recommended, therefore, because of its convenience where the greatest accuracy is not required, and where the angles of rotation remain below 100°. In the Landolt method, ordinary white light is used, and by aid of proper absorbing media all colors are removed, within rather narrow limits, except the one desired, which depends, of course, on the nature of the absorbing substance employed If now, rotation measurements are made with these rather homogeneous colors, the rotations found must correspond, according to §147, with some definite optical center of gravity, which depends simply and alone on the relative distribution of brightness in the spectrum of the color in question, assuming that the rotations are measured by a Lippich instrument, and that the active substance absorbs all wave-lengths of this color uniformly *Therefore, since the optical center of gravity is determined by the source of white light, and the absorbing media, and changes with both, the directions given by Landolt for preparing the ray filters must be followed with the greatest exactness if the measurements of different observers are expected to be comparable with each other* If modifications are adopted, the new optical center must certainly be defined and measured The Welsbach lamp serves as a source of white light for these ray filters, and as absorbing media solutions of only such substances are employed as are found in commerce in sufficiently pure condition. The solutions are filled into cylindrical glass cells of about 4 cm. diameter which consist of rings with plane glass plates cemented to them. One style of cell contains two compartments, each having an internal thickness of 20 mm., while another style has three divisions of 20, 15, and 15 mm thickness Each compartment is supplied with an opening, which may be closed with a glass stopper, and which permits the filling with the solutions. The cells may be shoved i a metallic framework having square plates on the corners prevent rolling These ray filters[1] are always to be placed b tween the source of light and the illumination lens of the app ratus, and the zero point must always be found after they a placed in position. It should be determined anew for ea ray filter, even when the half-shadow of the instrument h not been changed (see §106). The five filters permit re yellow, green, light blue and dark blue to pass.

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[1] Landolt Sitzungsber d Akad., Berlin, 1894, p 923, Ber d chem. Ges., 27, 2872 (1894).

Red —In the production of this color, the hydrochloride hexamethylpararosaniline is used, which comes into commer under the name of crystal violet 5 B O, and the anhydrous ca tharides green crystals must be selected If 0.05 gram of th be dissolved first in a little alcohol and then diluted with wat to one liter, this solution filled into a cell 20 mm. deep gives spectrum which consists of a red band and a broad blue vio part. The latter may be completely absorbed by adding a lay of yellow potassium chromate solution 20 mm. thick, and co taining 10 grams in 100 cc The red band now remaini begins with the wave-length about 718 $\mu\mu$, and ends sharp at 639 $\mu\mu$ The half-shadow of the instrument may be small as about 3°.

Yellow —A solution of 30 grams of crystallized nickel su phate in 100 cc., in a layer of 20 mm thickness, absorbs on the red rays and permits all others to pass If a cell 15 mm deep is added, containing potassium monochromate soluti with 10 grams in 100 cc., the blue and violet are taken ou leaving only orange-yellow and green The last of these colo may be absorbed by means of a potassium permanganate sol tion containing 0.025 gram in 100 cc., and used in a 15 mm layer. The spectrum is now reduced to a narrow orang yellow band which still shows a little red light and embrac the wave-lengths from 614 $\mu\mu$ to 574 $\mu\mu$. As the thr absorption solutions weaken the light materially, it is nece sary to employ a half-shadow of 8° to 10°.

Green.—For this, a combination of potassium monochroma with cupric chloride is used. A solution of 60 grams $CuCl_2 + 2H_2O$ to 100 cc in a 20 mm. layer allows, practicall only green and blue rays to pass. The last may be absorbed by a 20 mm. layer of a potassium monochromate solution containing 10 grams in 100 cc., and there remains then a broad green band on the edge of which there is still a little blue. This band embraces the wave-lengths from 540$\mu\mu$ to 505$\mu\mu$. The half-shadow must amount to 3° or more.

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[1] Obtainable from Schmidt and Haensch, Berlin

Light Blue.—In the production of this color there is used the compound known in commerce as double green S F, which is a combination of chlormethylhexamethylpararosaniline hydrochloride with zinc chloride, and which appears as a glittering bronze-colored powder. An aqueous solution of 0.02 gram of the color to 100 cc gives in a 20 mm. layer a spectrum consisting of a narrow red band with a broad green and a light blue part, the dark blue is absorbed. With a blue vitriol solution containing 15 grams in 100 cc. in a 20 mm. layer, the red band may be absorbed, but it is not possible to so remove the green light that light blue of sufficient intensity alone remains. The light left is, therefore, a combination of green rays of wave-lengths 526$\mu\mu$ to about 494$\mu\mu$, and of light blue rays from 494$\mu\mu$ to 458$\mu\mu$. As a result, no uniform color is found in the field of view of the polarization instrument, but the change of shade on turning the analyzer to and fro may still be followed. The half-shadow may be reduced to about 3°.

Dark Blue.—This color is obtained by a combination of solutions of crystal violet 5 B O, with 0.005 gram in 100 cc. and blue vitriol with 15 grams in 100 cc., both used in cells 20 mm. deep. The last solution absorbs the red rays which the aniline color passes and there remains only dark blue light of wave-lengths 478 to 410$\mu\mu$. Because of the low intensity of the light, a half-shadow of about 8° must be taken.

The absorption solutions, with the exception of the permanganate, are permanent, but it is advisable to keep the supply of the aniline colors in the dark, and to renew the filling in the cells holding them from time to time. But the permanganate solution must be freshly prepared, since it easily suffers decomposition.

As the rotation dispersion of quartz is pretty accurately known, the optical centers of gravity of the five colors from the ray filters may be found by the aid of quartz plates, according to § 148. Landolt has done this and has found that the five optical centers are near the Fraunhofer lines, C, D, E, F, and G. The following table shows the exact values:

Color filter.	Optical center of gravity in $\mu\mu$	Fraunhofer's lines	Wave-lengths in $\mu\mu$
Red = *rd*	665.9	*C*	656.3
Yellow = *yl*	591.9	*D*	589.3
Green = *gr*	533.0	*E*	527.0
Light blue = *lb*	488.5	*F*	486.1
Dark blue = *db*	448.2	*G*	430.8

These relations then obtain for the rotations α with quartz plates:

$$\begin{aligned} 1.032\ \alpha_{rd} &= \alpha_C \\ 1.010\ \alpha_{yl} &= \alpha_D \\ 1.026\ \alpha_{gr} &= \alpha_E \\ 1.011\ \alpha_{lb} &= \alpha_F \\ 1.091\ \alpha_{db} &= \alpha_G \end{aligned}$$

By aid of these equations it is, therefore, possible to reduce rotations found by the ray filter method to those which obtain for the corresponding Fraunhofer lines, and this may always be done if the active substance has about the same rotation dispersion as quartz.

The following table contains the data showing the preparation of the filter solutions, along with their optical centers of gravity and the corresponding rotations for 1 mm. of quartz at 20° C.

Color	Thickness of layer in mm	Aqueous solutions of	Grams of substance in 100 cc of sol	Optical center in $\mu\mu$	Rotation for 1 mm of quartz
Red	20 20	Crystal violet 5 B O Potassium monochromate	0.005 10	665.9	16.78°
Yellow	20 15 15	Nickel sulphate, $NiSO_4 + 7$ aq Potassium monochromate Potassium permanganate	30 10 0.025	591.9	21.49°
Green	20 20	Copper chloride, $CuCl_2 + 2$ aq Potassium monochromate	60 10	533.0	26.85°
Light blue	20 20	Double green S F Copper sulphate, $CuSO_4 + 5$ aq	0.02 15	488.5	32.39°
Dark blue	20 20	Crystal violet 5 B O Copper sulphate, $CuSO_4 + 5$ aq	0.005 15	448.2	39.05°

159. The Arons-Lummer Mercury Lamp.—The simplest method of determining rotation dispersion would be by aid of the Lippich half-shadow apparatus, if one had the means of producing a sufficiently large number of homogeneous lights of different wave-lengths. In §155 we have referred to a number of sources of homogeneous light besides sodium light, but they all have this disadvantage that their luminosity is too slight to make accurate observations possible. But, as a matter of fact, since there is need of homogeneous lights of great intensity for polarimetric work it may be safely assumed that before long this want will certainly be supplied This end might be reached, for example, just as du Bois produced an intense sodium light (§146), by forming similar pencils of salts of other metals as lithium, thallium, potassium, strontium, etc It would be a great advance to secure a sufficiently bright cadmium light, since according to Michelson[1] the four lines found in the red, green, and blue portions of the spectrum (643 8, 508 6, 480.0, 467 8 $\mu\mu$) have an extremely constant optical center of gravity. At the present time we have, in addition to the sodium light, only one other source of homogeneous light of great intensity, and this is the Arons mercury light

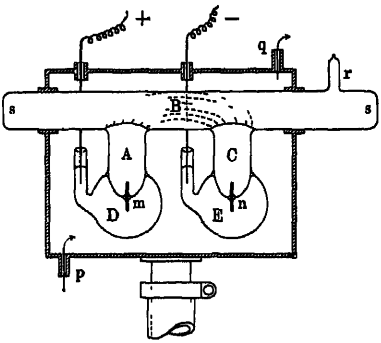

Fig 74

The mercury lamp constructed by Arons[2] and improved later by Lummer,[3] is shown in Fig. 74[4] The cylindrical tube B, with plane ends s, is connected near the middle with the two short vertical tubes A and C, which are closed below and furnished with platinum wires m and n, fused into the glass, a small tube is fused to B at r. The tubes A B C are cleaned and dried, A and C are filled with mercury, r is drawn out, and then, after exhaustion of B by a mercury pump, is sealed by melting. If a current from about thirty storage cells is led through m and n into A and B, and temporary contact is made by shaking the mercury, the arc light of this metal is produced which continues to play quietly after the apparatus is brought to rest with B in horizontal position The whole section of B is filled with a very intense grayish white light, which, diffused from the matted walls of the tube, shines freely through the end surfaces s, and is the brighter the stronger the current employed. If currents up to 10 amperes are used the glass at the contacts m and n must be protected from overheating. This is provided for by the little vessels D and E melted on to the lower ends of A and C, and which are likewise filled with mercury, so that the platinum wires m and n dip into this metal on each side. The current is led to the mercury by wires extending through the little tubes fused to the sides of D and E. As the tube B becomes very warm at the point where the arc is formed, if the current is at all strong, and may be broken through this heating effect, it must be furnished with a water-jacket to control the temperature and prevent cracking, which may be done, as shown in the figure, by leading water in at p and out at q. The two ends of the tube B project beyond the water-jacket, in order that the mercury, which vaporizes in large quantity, may not collect on the surfaces s, but on the side walls of B ; a constant variation in the intensity of the light is thus avoided A current of from 2 to 20 amperes may be sent through the lamp protected in this way by flowing water without running a risk of breaking it

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[1] Traveaux et mémoires du bureau international des poids et mesures, Tome, XI, Paris (1895) Michelson, Jour de Phys, [3], **3**, 5 (1894)

[2] Arons, Wied. Ann, **47**, 767 (1892).

[3] Lummer Ztschr für Instrum, **15**, 294 (1895).

[4] From Muencke, Berlin.

In spite of the appearance of continuity in the light arc the discharge is a discontinuous one This accounts for the fact that notwithstanding the low tension of about 17 volts at the mercury electrodes an electromotive force of at least three times this is required to produce the arc The arc exhibits a line spectrum of extraordinary strength But only a few lines are important for polarimetry. The line 546.1 $\mu\mu$, in the yellowish green is remarkably strong. If it is desired to illuminate the polarization apparatus with this light, it must of course be separated from light of all other wave-lengths produced at the same time, which may be best accomplished by the method of spectrum purification explained in §149. Two rather bright lines are found in the yellow with wave-lengths 579.0 and 576.9 $\mu\mu$; as these lie so close together a very great dispersion must be employed if they are to be actually separated and used in polarimetric measurements. But there is really no need of this, as in the immediate neighborhood of these lines the much stronger sodium lines are found. Finally the blue line, 435.9 $\mu\mu$, of the mercury arc light may be used; but as this is rather dark a large half-shadow angle must be taken so that the measurements made are not very accurate. From the above it is seen that the line in the yellowish green, 546.1 $\mu\mu$, is the only one applicable in polarimetry

As regards the constancy of the optical centers of gravity of the brighter spectrum lines formed by the mercury lamp one must stand in a skeptical attitude until fuller data are published concerning them. The spectrum of this light is made up of a remarkably large number of lines, Arons has determined no fewer than 32 lines between 623 and 404 $\mu\mu$ It is, therefore, hardly possible in polarimetric measurements to so far purify the four brighter lines mentioned above that light of adjacent lines may not also enter the apparatus It follows, therefore, as we know from §147, that the optical centers corresponding to measured angles of rotation can scarcely be stated with satisfactory accuracy Near the brightest line found in the yellowish green, 546.1 $\mu\mu$, there are found, for example, six other lines in the immediate neighborhood, and these have the wave-lengths 548, 545, 543, 537, 536, and 532 $\mu\mu$ The resulting optical center must vary, therefore, with the degree of dispersion employed in the spectral purification of the light. Furthermore, this center may change with the strength of current sent through the lamp, as it can hardly be assumed that the brightness of all the different lines increases in the same proportion (see also §150) In addition to this it appears, according to the statements of Arons, that with longer burning of the lamp the whole spectrum from about 543 to 503 $\mu\mu$ becomes of a dull green color, so that changes of the optical center with time are not impossible.

B. CONSTRUCTION OF THE POLARIZATION TUBES AND THE MEASUREMENT OF THEIR LENGTH.

160. Construction of the Tubes and Method of Closing Them by End Plates of Glass.—The tubes used with polarization instruments should always be made of glass. If in special investigations it is necessary to employ metal tubes, these should have a matted gold finish inside; but they have this drawback, that changes of length with temperature are much greater than with glass tubes. The tubes are commonly made 2 dm. in length, but shorter ones down to 1 dm and longer ones up to 1 meter are in use The inner diameter varies between 6 and 12 mm, and the thickness of the walls should be about 2 mm. *As shown in §96, the polarization tubes should have an internal diameter about 3 mm. greater than the polarizer and analyzer diaphragms of the instrument; if they have not, the latter should unquestionably be decreased.* The ends of the tubes are carefully ground off plane and care must be taken to have the two polished surfaces parallel to each other and vertical to the axis of the tube. The angle formed by the two ground surfaces should be always below 10′ For tubes not more than 2 dm. in length this angle may be measured very conveniently and accurately by aid of the Abbe spectrometer.[1] If the angle is of considerable size, it may be recognized in the following manner. The observation tube, filled with water, is closed with plane parallel cover glasses, placed in the polariscope and brought into focus with the telescope. If the tube is now rotated on its axis the field of view changes in shade if this angle is large.

The tubes are closed always with plane parallel glass plates. To accomplish this, each end of the tube is supplied with a brass setting on which a cap with a diaphragm may be screwed and this serves to press the glass plate against the end of the tube As the cover glasses should lie on the ends of the glass tubes only, the latter should project a trifle beyond the brass setting, the wedge-angle of the cover glasses should not exceed 5′; the exact angle may be measured by the Abbe spectrometer as before In order to prevent too great a pressure on the cover glasses when they are pressed home by the screw cap, a ring of rubber or soft leather is placed between the glass and the cap. *But, notwithstanding this, the cover glass must not be pressed too hard, because double refraction in the glass may follow through pressure, and this will destroy the uniformity of the field, and may easily give rise to a zero-point displacement in the instrument, amounting to several minutes.* As furthermore, without application of pressure and on account of internal strains in the glass, rotations of a minute or more may be caused by the cover plates, it is necessary in all accurate work to give very particular attention to the character of these plates; in saccharimetery, the cover glasses alone may lead to errors of several tenths of a Ventzke degree. Errors may be wholly avoided by noting first the reading with the empty tube and cover glasses in place, and then of the tube filled through a side opening with the liquid to be investigated; by subtracting the first reading with its proper sign from the second, the correct result is reached.

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[1] See Kohlrausch Praktische Physik, 1896, p 178

To exclude the possibility of making the cover glasses optically active by too strong pressure on the screw cap, observation tubes with the Landolt closing device are now very frequently used. With this the glass plates are not pressed against the tube by the motion of the screw cap, but by means of a cap held down by a spring

In the investigation of beet-juices, the Pellet tube[1] for continuous polarization, shown in section in Fig 75, is frequently used. It is commonly made of metal, is closed at A with inside screw caps, and at each end has a side tube entering near the glass cover plates A funnel is attached to one of these tubes and to the other a piece of rubber tubing with properly bent glass tube, so that the solution at any time in the polarization tube may be completely forced out by the pressure of fresh liquid poured into the funnel. In this way, a great many polarizations may be rapidly carried out in the same tube, one after the other; but the actual observation

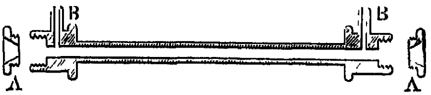

Fig 75

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[1] Pellet Ztschr für Rübenzucker-Ind, 41, 338 (1891). The tubes may be obtained from Schmidt and Haensch

must not be made until the old contents of the tube are fully expelled by the new, which is the case when the cloudy striations, noticed at first, have completely disappeared.

When the telescope is focused after putting a filled observation tube in the instrument, the field of view must be sharply and uniformly clear throughout its whole extent, the outside edge and the dividing lines of the fields as well; only when this is the case is it proper to begin the observations. If the adjustment does not remain sharp on turning the tube it shows either that the solution was not homogeneous or that the tube was not clean.

If qualitative observations only are to be made, glass troughs, as shown in Fig. 76, may be recommended.[1] The cover, furnished with a button, may be taken off, while the other parts are fastened together with easily fusible glass. These troughs may be placed in the gutter h (Fig 45) of the Lippich-Landolt apparatus.

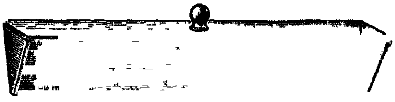

Fig. 76

161. Water-Jacket Tubes and Water-Heating Apparatus. - Tubes furnished with instruments do not ordinarily have a water-jacket, the contained liquid is, therefore, exposed to the prevailing air temperature. But as the room temperature is variable to the extent of at least ± 3°, and as the rotating power of most substances is largely modified by heat, it is necessary in all accurate measurements to control the temperature of the liquid during the observations. This may be done by surrounding the glass tube with a brass jacket 3 to 5 cm. in diameter and allowing a current of water to flow through the space between, the water having previously been brought to the desired temperature in a reservoir. A jacketed tube is shown in Fig. 77[2] The tube proper consists of glass and to the middle of it is fused the thermometer tubulure A, which at the same time may be used in filling the observation tube. The brass jacket for the water circulation has two projecting tubes, B and C, which serve for the inflow and outflow of the water. After pouring in the solution the tubulure A is closed with a ground glass stopper D, through the larger central opening in which a thermometer E is introduced. This thermometer has a wide part near the bottom which is ground to fit the opening air-tight The mercury reservoir of the thermometer is, therefore, immersed in the liquid, and it must project so far into the latter that its lower end is just visible in looking through the observation tube The glass stopper D has a second opening at one side, into which a fine glass tube is cemented, and to this a bit of rubber tubing, F, may be attached A part of the air in A, above the liquid, escapes through this when the thermometer is inserted; more may then be sucked out and F closed by a clamp. The thermometer E is graduated in tenths, and of course its accuracy must be determined before the observations. It is safest to have the thermometer tested by the Physikalisch-Technischen Reichsanstalt at Charlottenburg, and corrected say from 5°–5°.

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[1] From Leybold, in Cologne

[2] From Schmidt and Haensch, Berlin

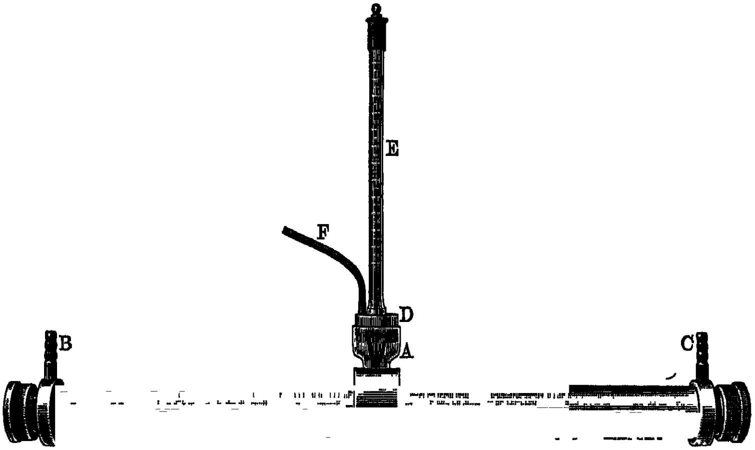

Fig 77

A water-heating apparatus, in which the water to flow through the jacket of the observation tube is brought to the right temperature, is shown in Fig 78.[1] It is made of sheet zinc, but has a copper bottom, and to prevent cooling or warming by the air is covered above and on the sides with flannel The removable cover is furnished with two small openings.

[1] From Rohrbeck, Berlin

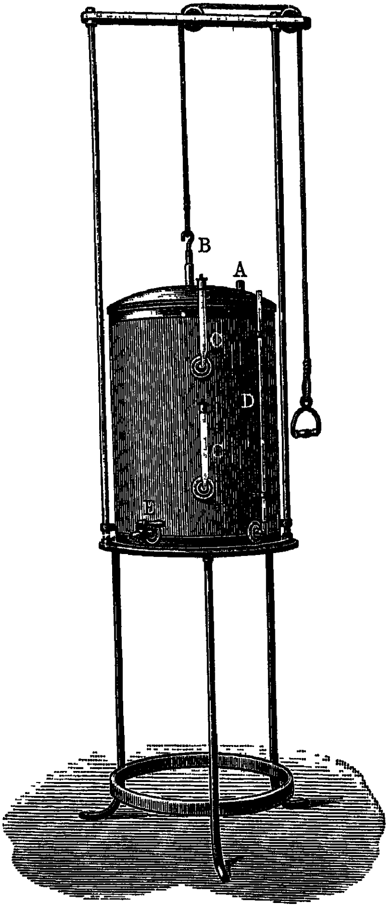

Fig 78

Through one of these, A, the reservoir may be filled with water, while the rod of the stirrer works through the other. This latter consists of a perforated disk filling the whole section of the reservoir, with a piece cut out at the right point to avoid striking the ends of the thermometers C, bent at right angles, the rotation of the stirrer is prevented by two vertical guides placed on the inner walls of the reservoir. D is a glass tube to show the level of the water, and E the exit tube, with a stop-cock, which may be connected with the water-jacket of the polarization tube by means of rubber. A second large opening, not shown in the figure, and likewise furnished with a stop-cock, serves, when necessary, for the rapid discharge of the water The reservoir which is supported on an iron stand may be warmed by means of a Bunsen burner or by a warm coil. Before beginning an observation, water is allowed to flow about fifteen minutes through the water-jacket and continued during the readings. The temperature t, which is the mean of all the readings of the thermometer in the polarization tube during an observation, is then that temperature to which all other factors must be reduced, as will be seen by the following paragraph.

162. Calculation of the Specific Rotation, with Consideration of the Effect of Temperature.—If α is the angle of rotation of the solution of an active substance, l the length of the observation tube, p the percentage strength, and d the specific gravity, then, according to §2, the specific rotation is $[\alpha] = \frac{100\alpha}{lpd}$. We shall write this equation in the shorter form $[\alpha] = f(\alpha, l, p, d)$, that is, $[\alpha]$ is a function of α, l, p, and d. With the exception of p, the quantities α, l, and d are variable with the temperature t, so that $[\alpha]$ also must vary with t. If we express this dependence on the temperature by the index t, then $[\alpha]_t = f(\alpha_t, l_t, p, d_t)$. If we give t the definite value t_0 then the specific rotation for the temperature t_0 is expressed properly only by the equation, $[\alpha]_{t_0} = f(\alpha_{t_0}, l_{t_0}, p, d_{t_0})$; the quantities α, l, and d must all be determined for the temperature, t_0. It must, therefore, be considered as absolutely improper, as is unfortunately often the case to find α and l, for example, for 20°, and d for 17.5°, and to calculate an $[\alpha]$ with these values, because the $[\alpha]$ so found corresponds naturally to no definite temperature Now, the coefficients of expansion corresponding to l and d are easily determined (in fact are mostly already known), so that l and d may be readily found for any temperature. *Therefore, the temperature at which α is measured, is the one which must be taken as the basis for the whole calculation of* $[\alpha]$. If now the rotation is found at the temperature t_1, (α_t), then l_{t_1} and d_{t_1} must be calculated to correspond, and finally $[\alpha]_{t_1} = f(\alpha_{t_1}, l_{t_1}, p, d_{t_1})$, in this way the specific rotation for the temperature t_1 is determined. If, next, α_{t_2} is observed in the same manner, we obtain $[\alpha]_{t_2} = f(\alpha_{t_2}, l_{t_2}, p, d_{t_2})$ We obtain in this way a clear idea of the dependence of $[\alpha]$ on t, and finally after calculating the temperature coefficient of $[\alpha]$, we are able to reduce all the observed values of $[\alpha]$ to one and the same temperature, usually to 20°. It must further be mentioned *that the specific gravity is always referred to water at 4°, the choice of any other temperature* (0° or 17.5°) *is certainly to be condemned, since water at 4° is the basis of the metric system of weight.*

163. Schmidt and Haensch Control Tube.—The Schmidt and Haensch control observation tube,[1] the use of which was referred to in §128, is illustrated by Fig. 79. The tube A may be moved, in telescope fashion, into the tube B which it fits very accurately, a leather washer being added at C to make the joint perfectly tight. The ends D and E are closed by the ordinary screw caps. The motion of the tube A is accomplished by pinion and rack mechanism F; on the latter there is a millimeter scale which works over the vernier G, attached to B, so that tenths of a millimeter may be read off directly. The funnel H, which is detachable, serves to take up the excess of liquid expelled on contraction of the tubes. Instead of closing the tube A at D it may be closed at the other end at J by screwing in a diaphragm with a plane parallel glass plate; in this arrangement the whole tube is shorter by the length D J, than when the end is taken at D. On this principle (with diaphragm at J) tubes may be constructed whose length may be decreased to zero. For saccharimeters which are made to take in very long tubes, such an arrangement would be very advantageous as it would permit a determination of the whole error of the quartz wedge by use of a single sugar solution. For the ordinary short saccharimeters, the use of such a tube, which may be shortened to zero, is not to be recommended, since the determination of errors is less accurate, the shorter the tube in fully extended condition.

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[1] Schmidt and Haensch · Ztschr für Instrum, 4, 169 (1884).

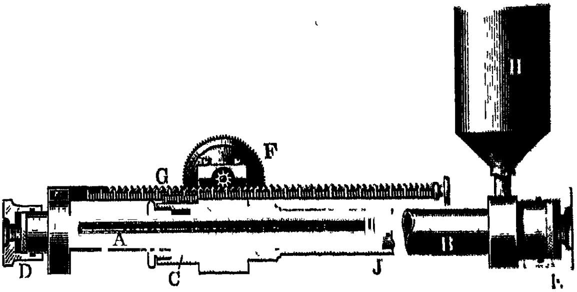

Fig. 79.

It may be remarked regarding the practical use of the control observation tube, that the solution cannot be introduced through the funnel H This should be removed and the orifice closed by the metallic stopper furnished with the tube. The cap E is removed, the tube fully extended, and then the solution is poured in. After filling and closing E the tube is brought into horizontal position, H is attached, and then the tube is shortened a little and a further small amount of liquid poured into the funnel. To prevent too much evaporation it is recommended to cover the latter with a screw top which has a very small opening to permit the escape of the air.

164. Measurement of the Tube Length.—The statement of the manufacturer is commonly taken as regards the length of the tube. But for all accurate work this length must be known with certainty to within 0.1 mm., and it is, therefore, desirable to have means of measuring it one's self. A measuring instrument designed by Landolt for this purpose is shown in Fig. 80.[1] It consists of a metallic bar, A, divided into millimeters, on the lower end of which, at a, there is a sharp knife edge The handle c, of wood, may be fixed at any point desired The vernier b, provided with two knife edges, may be shoved along the bar with a little friction, and permits a reading to 0 1 mm. If the bar A is placed vertically with the edge a on a glass plate and then the vernier is shoved down until its two edges rest on the plate, the zero point on the bar and the zero on the vernier must agree, so that the reading zero is thus given. If the length of the tube B is to be found, one end is closed by a glass plate and screw cap, and then, in vertical direction, the measuring bar A is shoved down into the tube until the edge a touches the glass at the bottom Then the vernier b is brought down until its two edges touch the glass tube above, taking care that the bar A does not stand

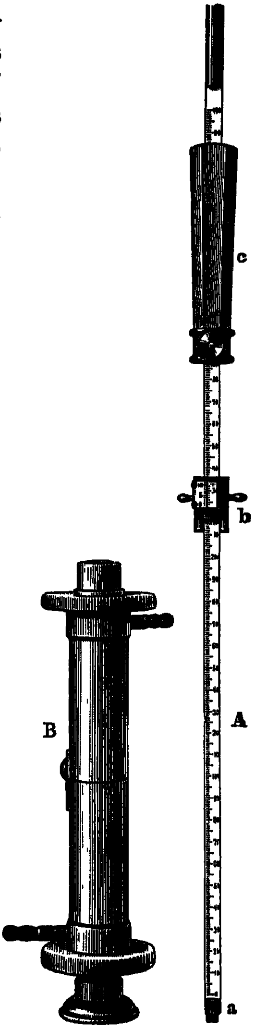

Fig. 80

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[1] From Schmidt and Haensch, Berlin.

inclined in the tube. The length is then read off. This determination is repeated several times, the tube being turned through 90°, 180°, and 270°, and the mean of all taken. If the length found is expected to be actually accurate within 0.1 mm., the correctness of the measuring bar must be previously determined, and above all the temperature of the bar must be considered.[1]

In all cases where it is desired to know the tube length more accurately than to 0.1 mm., the simplest plan is to have the measurement made directly in the Physikalisch-Technischen Reichsanstalt at Charlottenburg. The length of polarization tubes may be there accurately found by aid of a comparator to within 0.01 to 0.02 mm.

If the angle of rotation of a liquid is found at different temperatures the change in length of the tube must be taken into consideration. It is sufficient for this purpose to consider the linear coefficient of expansion of glass as $\beta = 0.000008$ for 1°, and for brass $\beta = 0.000019$. If the length of the tube at 20° be taken as l_{20°, then the length at t° is found from the equation,

$$\text{(I)} \qquad l_{t^\circ} = l_{20^\circ} + l_{20^\circ}\,\beta\,(t - 20).$$

If, for example, a glass tube measures exactly 200 mm. at 20°, its length, according to this, at 30° is 200.016 mm. The correction need, therefore, be considered only with long tubes and marked temperature changes.

C. DETERMINATION OF THE PERCENTAGE STRENGTH OF SOLUTIONS

165. **Reductions of Weighings to Vacuo.**—The determination of the percentage strength by weighing will be considered in what follows in such a manner as to make it as accurate as possible. If for special purposes, less accuracy is called for in the work, the procedure may naturally be easily simplified. As all weighings must be reduced to vacuo, the necessary formulas will first be stated. It must be assumed that these weighings are made on chemical balances which permit a mass determination which is accurate to about ± 0.1 mg.

A few remarks only need be made about the weighings themselves. The temperature of the weights, of the body to be weighed and of the air in the balance case, should differ but little from the air temperature of the room Do not place a vessel with calcium chloride in the balance case, as it is not possible to keep the air in the latter dry during the time of weighing, at most the calcium chloride may be used as a protection against rust when the balance is not in use. All weighings should be made by the method of vibrations, with a determination each time of the zero point and the sensitiveness of the balance; aside from its greater accuracy, weighings by the vibration method, when one is once accustomed to it, require less time than is necessary to accurately adjust the rider It is necessary to determine always three or five reversal points. In regard to a determination of the errors in the set of weights it is only necessary to compare one of the pieces with a normal set of weights;[1] the errors of all the others may then be found from this with sufficient accuracy The list of corrections should be pasted on the balance table, and at each weighing the sum of the errors in the weights used should be noted at once Further directions may be found in Kohlrausch's "Praktische Physik," 1896, 41 to 53.

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[1] The Physikalisch-Technischen Reichsanstalt at Charlottenburg makes tests of measuring rods and determinations of their errors in division.

In the reduction of the weighings to vacuo, the density of the air λ (the mass of 1 cc. in grams) at the time of weighing must be known The density of the air is a function of the temperature t in the balance case, of the barometric pressure, b, in millimeters to be reduced to 0°, and of the tension e of the aqueous vapor in the air ·

$$\lambda = \frac{0\ 001293}{1 + 0\ 00367\ t} \frac{b - 0.375\ e}{760}$$

As for North Germany e is usually between 3 and 15 mm., it is sufficient to take for the purpose $e = 9$, so that we have then,

$$\text{(I)} \qquad \lambda = \frac{0.001293}{1 + 0\ 00367\ t} \frac{b - 3.4}{760}.$$

The error in λ occasioned by variations in e amounts in the maximum to ± 0.000004. If the barometer is not measured on the same floor where the weighing is made, a correction must be made on b, since b decreases 0.1 mm. for an elevation of 1 meter. If t is observed accurately to 0.5° and b to 1 mm., then by aid of equation (I) the air density λ is obtained correctly to within about $\pm$ 0.000008. In the mean, λ is about 0.00119 and varies between the limits 0.00113 and 0 00125.

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[1] The Normal-Aichungscommission, at Berlin, makes such comparisons

To eliminate the error due to inequality in the arms of the balance, the body whose absolute mass is to be found is weighed first on the one pan and then on the other. If m_1 and m_2 are the weights used in the two cases to hold the body in equilibrium, then the right weight of the body in the air is:

$$\text{(II)} \qquad m = \frac{m_1 + m_2}{2}.$$

The mass so found is then to be reduced to the vacuum weight as above If s is the density of the body and σ the density of the weights, then the desired mass M of the body in vacuo is

$$M = m + m\lambda\left(\frac{1}{s} - \frac{1}{\sigma}\right),$$

or in better form for computation

$$\text{(III)} \qquad M = m + m\lambda\,\frac{\sigma - s}{\sigma s}$$

Ordinarily the weights are of brass, for which $\sigma = 8.4$ may be taken; the fact that the smaller weights are of platinum or other foil has no appreciable effect on the value of M. With reference to the densities, s, consult Landolt and Boernstein's Tables, 1894, p 114 to 234, from which with the numbers on p 10 the values for $\lambda\,\frac{\sigma - s}{\sigma s}$ may be taken

If m is the apparent mass of the body in the air of density λ, and m' the apparent mass of the body in air of density λ'; then follows from equation (III),

$$\text{(IV)} \qquad m' = m + m\,(\lambda - \lambda')\,\frac{\sigma - s}{\sigma s}$$

By means of this equation it is possible to reduce the mass found for any density of the air λ to any other density λ'

166. Preparation of Solutions by Weighing.—For this purpose it is advisable to use small flasks with wide neck and glass stopper, having a capacity of 20 to 150 cc (Fig. 81) After cleaning the flask with water and rinsing with alcohol, it is dried by forcing air for a long time through it Then, according to the last paragraph (II), its apparent mass m in the air of density λ will be found. Next, one of the components A of the solution is introduced into the flask; if a definite quantity of A is to be taken it is more convenient to use a coarse balance at first, and then by means of an analytical balance to find the exact weight According to (II) we have now the apparent weight n of the flask and substance in the air, with the density equal to λ'. After obtaining, according to (IV),[1] by aid of m, λ and λ', the apparent mass of the flask m' at the air density λ', then we have as the apparent mass n_1 of the substance A at the air density λ',

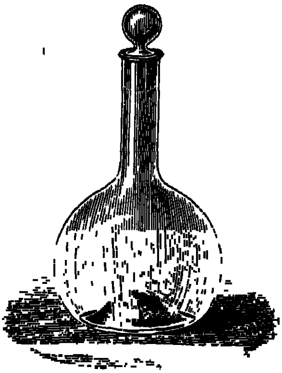

Fig 81

$$n_1 = n - m' ,$$

n_1 is reduced, according to (III), to the vacuum weight and we obtain then as the real mass M_1 of A,

$$M_1 = n_1 + n_1 \lambda' \frac{\sigma - s_1}{\sigma s_1} .$$

Then the second component B of the solution is brought into the flask and care is taken to make a homogeneous solution by shaking. Just as M_1 was found, we find now the true mass M of the solution composed of A and B, but we must substitute now in (III) in making the reduction, the specific gravity s of the solution The real mass, M_2, of the component B is then

$$M_2 = M - M_1.$$

We proceed in the same manner if still other components are to be added. If the solution contains the components A and B only, of which B is the solvent, then the percentage strength, p, of active substance A in the solution is

$$\text{(V)} \qquad p = \frac{100\, M_1}{M}.$$

It is to be observed that p, also the per cent. of the solvent,

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[1] The density of the glass may be taken as 2.5

$q = \frac{100\,M_2}{M} = 100 - p$, are quite independent of the temperature; the percentage amount p gives clearly the composition of the solution, the solution is completely defined through p only.

It is, therefore, advisable in following changes in specific rotation with increasing dilution of the solution, to represent the specific rotation as a function of p or q as is done on page 5, rather than as a function of the concentration If water is used as the solvent, it should be thoroughly boiled so as to expel all the air.

In this manner, when necessary, the percentage strength p may be found with very great accuracy. If, for example, the normal sugar solution so commonly used in saccharimetry, in which the amount of sugar is about 23.7 per cent, is accurately prepared by weighing and is then filled into the polarization tube, in which operation a little water is lost by evaporation, the actual percentage strength of the solution in the tube, after allowing for all systematic errors, may be given to within $^1/_{10,000}$ of its value; that is, accurately to ± 2 or 3 units of the third decimal place. But if the weighings are not reduced to vacuo, the percentage strength would be too large by one unit in the second decimal place.

167. Change in the Percentage Strength on Filtration of the Solution.—But this great accuracy in the percentage strength no longer obtains if, on account of turbidity, one is obliged to filter the solution, because then by partial evaporation of the solvent, the percentage amount of the non-volatile constituent is increased. In order to obtain an estimate of the extent of the error so caused some experiments were made, and partly in this way that the whole filtering apparatus was placed on the balance, and partly by determining the strength before and after filtration Plaited filters of Swedish paper were used and the funnels and vessels were kept covered as well as possible

Aqueous solutions: *a.* 43 131 grams of water filtered in four minutes and lost 0.019 gram by evaporation. Air temperature, 18°. 99.614 grams of water filtered in 11 minutes with a loss of 0.041 gram Temperature, 20° According to this, in the filtration of 40 to 100 grams of a 10 per cent. solution, the percentage strength would increase by 0.004. *b.* In the filtration of 50 cc. of an aqueous solution of silver nitrate, which was completed in three minutes, the percentage strength increased from 9.708 to 9.713. The temperature was 20°. The increase is 0.005, which agrees with the first determinations.

Alcoholic solutions · *a.* 31.007 grams of 94 per cent. alcohol filtered in four minutes and lost 0.067 gram by evaporation, at a temperature of 18°. 71 494 grams of the same alcohol filtered in ten minutes, at 19°, and lost 0.114 gram. If the above alcohols had contained 10 per cent. of active substance, this amount would have been increased in the first filtration to 10.019 and in the second to 10.014 per cent. *b.* 50 cc. of a solution of silver nitrate in 78 per cent. alcohol filtered in ten minutes, at 23°, and increased in strength from 9.686 to 9.714 per cent. in one experiment, and to 9.736 per cent. in another; that is, by 0.03 and 0.05.

If we may assume that the evaporation is independent of the percentage strength and proportional to the amount of liquid filtered, which is only approximately true, it may be estimated that in aqueous solutions after filtration, the amount is increased by about 0 005 for each 10 per cent. of substance, and for alcoholic solutions by about 0.03 to 0.05

These increases in percentage strength may, therefore, be quite considerable for concentrated solutions, and if alcohol serves as the inactive solvent the first decimal place even may be wrong by several units. *Filtration, therefore, should be avoided as far as possible*

D. DETERMINATION OF SPECIFIC GRAVITY

168. Construction and Use of the Pycnometer.—The specific gravity or density of a body is the relation of its mass to the mass of the same volume of water at 4° The choice of any other temperature is inadmissible. If the body is homogeneous the specific gravity is at the same time the mass of the unit of volume, the gram and cubic centimeter being naturally used together.

The densities of solid bodies are important in polarimetry only so far as employed in the reduction of weights to vacuo, and the methods of determination need not be discussed here.

Reference is made to Kohlrausch's "Praktische Physik," 1896, p. 57 to 60, and it may be remarked further that for the cases coming into consideration here the floating method devised by Retgers gives the best results.

The densities of liquids may be found by aid of the pycnometer, the Mohr balance or the aerometer But the last two methods require larger quantities of liquid and may be applied to solutions only when the evaporation of the solvent is slight; but as they are easily subject to many systematic errors and do not possess at all the accuracy which is reached without difficulty with the pycnometer, the Mohr balance and the aerometer are only used in technical work for approximate determinations, while for scientific investigations the pycnometer alone may be employed

With the pycnometer the mass of a definite volume is determined. Among the many kinds of pycnometers that of Sprengel gives unquestionably the most accurate results. The most practical form is shown in Fig. 82 The vessel A holds about 15 cc. and is made of rather thin glass. The two capillary tubes B and C, bent in the middle, are fused to the upper end of A. The extremities of these are ground. The internal diameter of the capillaries is not the same; B, which has a mark at D is about 0.9 mm, while C is smaller and about 0.4 mm. in diameter. In order to be able to hang the pycnometer on the balance it is provided with a platinum loop E, as shown in the figure. To prevent evaporation during weighing, and possible loss of liquid by expansion with increase of temperature, the ends B and C may be closed by the two ground glass caps F and G To distinguish it from G the cap F is marked by a blue glass bead at its end since this one is to be put on the capillary marked at D. To facilitate drawing in the liquid the bent glass tube H with ground end may be attached to the wider capillary B, and to the narrow capillary C, the bulb J, with ground neck, to which a bit of rubber tubing is attached. The definite volume of the pycnometer, which is always used filled, reaches from the point of C to the mark D and changes only by expansion of the glass with the temperature.

The pycnometer is cleaned by washing with distilled water

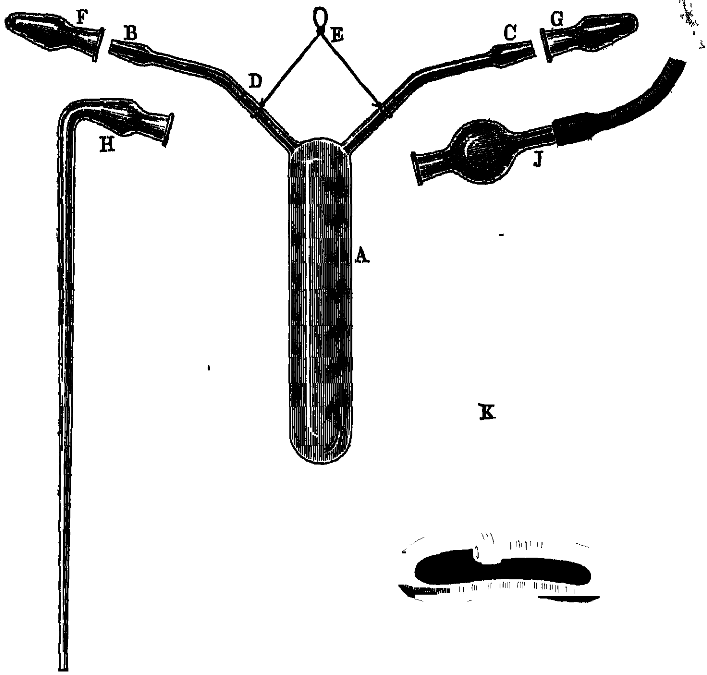

Fig 82

and alcohol, the latter being vaporized finally by a current of air. The apparent mass of the empty pycnometer with the two glass caps F and G in the air, is then a constant to within about ± 0.2 mg., the changes on account of variations in the density of the air taken into consideration In the determinations of specific gravity it is not necessary to make allowance for variable air density as may be seen in the following calculation of errors for the specific gravity 1 1. The greatest deviation in the density of the atmosphere from its mean value of 0.00119, or 0.0012, is about ± 0.00005 As the water weight of the pycnometer is not commonly redetermined with every new specific gravity test the density of the air can cause a maximum error of about ± 9 units in the fifth decimal place in the determination of liquid densities; but it is assumed here that the empty pycnometer is reweighed before each determination, and that, therefore, its apparent mass in the air can be brought into the calculation with an error of at most ± 0.05

mg. Leaving out of consideration rare exceptional cases, the error in the liquid density by variations in the air density is, as a rule, less than 4 units in the fifth decimal place. As will be further seen below, all other uncertainties taken together may produce an error of about ± 2 units in the fifth decimal place. By adding the error of four units on account of uncertain air density the final error is 6 units, that is, *the error in a specific gravity determination is ordinarily only ± 6 units in the fifth place, even when the variable air density is left out of consideration;* this degree of accuracy in specific gravity determinations is sufficient for all polarimetric work. It is likewise unnecessary, in specific gravity tests, to make double weighings in determining the apparent masses in the air; if the weighing is always made on the same side the inequality of the balance arms is completely eliminated, since specific gravity is the relation of two masses; it is assumed, of course, that the relation of the two arms is sufficiently constant, which, for the small loads here taken, should always be the case in a good balance.

The pycnometer is filled with distilled water, reboiled to free it from air, and brought into a bath of constant temperature. A cylindrical glass dish with a capacity of several liters may be used as a water-bath; it should be placed in a round wooden vessel, the bottom of which is lined with a thick layer of cotton, and the space between the sides of the glass and wooden vessels should be also packed with cotton. For temperatures between 15° and 25° the temperature of the water-bath will then remain constant to within a few hundredths of a degree. A standard with two movable arms is attached to the wooden vessel. One supports the holder K (Fig. 82), which may be made of a bent glass rod or of a thick piece of covered copper wire, while the other supports a thermometer. The pycnometer is hung in the holder K, and is immersed in the water of the bath to the level of the mark D The thermometer, graduated in tenths, the accuracy of which has been previously tested (see §161) is hung as close as possible to the pycnometer and care is taken to have the mercury in the bulb about at the level of the middle of A. If the water-bath is colder than the pycnometer, the liquid in the latter contracts on immersion in the bath, but only in the wider capillary B, while the na rower one C remains always full If the water retreats beyond the mark D, a drop of water on a glass rod is held to th point C This is immediately drawn into the narrow capillar and the mass of water moves up in the wider tube B. The the outside ends of B and C are carefully cleaned by bits o filter-paper. After about ten minutes, the pycnometer an contents will have come exactly to the bath temperature, whic may be recognized by the fact that the liquid meniscus in th capillary B remains constant in position. After the temperature on the thermometer is read as accurately as possible, C is touched with a bit of filter-paper which causes the meniscus in B to move toward D; at the moment in which the middle of the meniscus just reaches D the filter-paper is withdrawn and the adjustment is completed; in the adjustment the eye is held so that the mark D appears as a line. Finally, the narrow capillary C is first closed with the cap G and then B with the cap F. When this is done the pycnometer is taken from the bath and dried with a soft linen cloth, and then it is placed on the balance where its apparent mass in air is determined. If from this the apparent mass of the empty pycnometer be subtracted, the difference gives the apparent mass in air of the water which fills the pycnometer at the temperature of the bath. This apparent mass, which depends on the temperature only, is a constant for the pycnometer used and need not be found anew for each specific gravity determination After some practice such a degree of accuracy may be reached that with repeated adjustment and reductions to the same temperature, the apparent water masses will not vary by more than 0 1 to 0.2 mg. But it must be remembered that 15 grams of water weighed in the air may vary about ± 0 6 mg in maximum by reason of changes in the air density. The above calculation of errors is based on these relations.

After cleaning the pycnometer with alcohol and drying it, it is filled with the liquid whose specific gravity is to be found. All manipulations are now the same as before with water. The adjustment and weighings are made at least twice to avoid possible errors. By subtracting the apparent mass of the empty pycnometer from that of the filled, the apparent mass of the liquid in the air is obtained. By repeated weig ings, and reductions to the same temperature, this should va at most by 0.1 to 0.2 mg.

169. Calculation of the Specific Gravity.—The following is t calculation of the specific gravity. We represent by

W_0, the apparent mass of the water in the air at the te perature t_0,

F, the apparent mass of the liquid in the air at the te perature t;

Q_0, the specific gravity of the water at the temperature t

3β, = 0.000024, the coefficient of cubical expansion glass;

λ, = 0.0012, the air density,

d_t, the density of the liquid at the temperature t, referr to water at 4°.

Then

$$d_t = \frac{FQ_0}{W_0} + \frac{FQ_0}{W_0} 3\beta (t_0 - t) - \frac{\lambda (F - W_0)}{W_0}. \tag{I}$$

In this, the first factor is the rough uncorrected specific gravit the second and third factors are corrections. The secon factor corrects the specific gravity on account of temper ture changes, and the third comes from the reduction of th weights to vacuo. As already explained in the last paragrapl we obtain the specific gravity with the pycnometer to withi about ± 6 units in the fifth decimal place. The specifi gravity may be given, therefore, to the fifth decimal, but th first factor must be calculated with seven-place logarithms

If, in each weighing, the air density, λ, is found accordin to equation (I) (§165), then

$$d_t = \frac{F' Q_0}{W_0'} + \frac{F' Q_0}{W_0'} 3\beta (t_0 - t), \tag{II}$$

in which W_0' and F' are the true masses of the water and th liquid, reduced to vacuo, by aid of equations (I) and (III (§165).

The values of the specific gravity, Q_0, of water at differen temperatures of the hydrogen thermometer are found from th following table, which contains the mean values of Thiesen Scheel and Marek. The numbers are accurate to about fiv units in the sixth decimal place, as may be seen by comparison with the latest observations.[1] A fuller table is found in Landolt and Boernstein's Tables, 1894, p. 37.

t_0	Q_0	t_0	Q_0	t_0	Q_0
0°	0 999 874	18 0°	0.998 628	21.0°	0 998 023
1	930	1	609	1	001
2	970	2	590	2	0.997 979
3	993	3	571	3	957
4	1.000 000	4	552	4	935
5	0 999 992	5	533	5	913
6	969	6	514	6	890
7	931	7	495	7	868
8	878	8	476	8	846
9	812	9	456	9	823
10	731	19.0	437	22 0	800
11	637	1	417	1	778
12	530	2	397	2	755
13	410	3	377	3	732
14	277	4	357	4	709
15	132	5	337	5	685
16	0 998 976	6	317	6	662
		7	296	7	639
17.0	808	8	276	8	615
1	790	9	255	9	592
2	772				
3	755	20.0	235	23	568
4	737	1	214	24	326
		2	193		
5	719	3	172	25	073
6	701	4	151	26	0 996 811
7	683			27	540
8	664	5	130	28	260
9	646	6	109	29	0.995 971
		7	087		
		8	066	30	674
		9	044	31	368

If, in the equations (I) and (II), $(t_0 - t)$ amounts to but a few degrees, it is sufficient to take for 3β the mean val 0.000024 But it is always better to find the coefficient of e pansion, 3β, of the glass of the pycnometer by direct expe ment. For this purpose, the pycnometer is weighed, fill with air-free water at two different temperatures. If, for e ample, several determinations are made at about 10° and 30 3β may be found accurately within about 2 per cent. If th two temperatures are t_1 and t_2, with $t_2 > t_1$, Q_1 and Q_2 the co responding specific gravities of water, W_1 and W_2 the masse of the water contained in the pycnometer at temperatures and t_2, then

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[1] Thiesen, Scheel, and Diesselhorst Wied Ann., 60, 340 (1897), 'Die Thätigkeit der Physikalisch-Technischen Reichsanstalt,'' Ztschr für Instrum., 17, (1897)

$$\text{(III)} \qquad 3\beta = \frac{W_2(Q_1 - Q_2) - Q_2(W_1 - W_2)}{W_1 Q_2 (t_2 - t_1)}$$

Although the numerator may be simplified to $W_2 Q_1 - W_1 Q$ it is still more convenient in working with definite numbers t use the above form of the equation. If the density of the ai remains constant throughout the experiment, it is not necessary to reduce the weights to vacuo, as 3β is dependent onl on the ratio $W_2 \; W_1$

170. Variations in Specific Gravity with the Temperature.— In all more accurate polarimetric work, as shown in § 162, changes of specific gravity with the temperature must be known and, therefore, the coefficient of cubical expansion of the solution must be found. This is best done by aid of the pycnometer. Let this contain the mass of liquid F_1 at the temperature t_1, and at the higher temperature t_2 the mass F_2. If 3β is the coefficient of cubical expansion of the glass, then the mean coefficient of expansion of the liquid, γ, between t_1 and t_2, or also (with sufficient accuracy) the true coefficient for the temperature $\frac{t_1 + t_2}{2}$, is given in form suitable for calculation by

$$\text{(IV)} \quad \gamma_{\frac{t_1+t_2}{2}} = \frac{F_1 - F_2}{F_2} \frac{1}{t_2 - t_1} + \frac{F_1 - F_2}{F_2} 3\beta + 3\beta.$$

As γ is dependent on the ratio $F_1 \; F_2$ only, it is not necessary, constant air density assumed, to reduce the weighings to vacuo. If the temperature difference, $t_2 - t_1$, is taken as about 15°, the coefficient of expansion may be easily determined to within about 3 per cent., which is sufficient for all polarimetric work.

As far as the variation in γ with the temperature is concerned, we may assume this relation with sufficient accuracy for simple liquids as well as for solutions of definite percentage strength,

$$\text{(V)} \qquad \gamma_t = \gamma_{20^\circ} + a(t - 20),$$

in which a is a constant peculiar to the liquid. If, therefore, we find γ for two different temperatures, then we may calculate first the two constants γ_{20° and a, and next the coefficient of expansion for any desired temperature; it is required, therefore, to find the mass of the liquid in the pycnometer for at least three different temperatures.

For solutions, γ varies also with the percentage strength p of dissolved substance, so that γ must be written as a function of p and t in the form

$$\text{(VI)} \qquad \gamma = f + g\,p + h(t - 20) + i\,p(t - 20),$$

in which f, g, h, and i are four constants. If then the equation (V) is established first for the pure solvent, and then for a single solution of percentage strength p, the four constants may be found in a manner easily seen, and γ may then be calculated for any desired p and t. In case the equation (V) has been found for several solutions of different strengths, p, the four constants may be calculated by aid of the method of least squares[1]

As an example, we may take the expansion of a pure sugar solution in water. According to Schönrock[2] the dilation coefficient, γ, between 11° and 26°, of a sugar solution with percentage strength between $p = 0$ and $p = 30$, is given by the equation

$$\gamma = 0.000208 + 0.0000037\,p + 0.0000108\,(t - 20) - 0.00000019\,p(t - 20).$$

This formula gives the true coefficient of expansion accurately to within ± 0.000008

If the equation (VI) is found for γ, and the specific gravity d at the definite temperature t' has been determined, the specific gravity for any other temperature t may be found from the equation

$$\text{(VII)} \qquad d_t = d_{t'} + d_{t'}\,\gamma_{\frac{t+t'}{2}}\,(t' - t).$$

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[1] See Kohlrausch, "Praktische Physik," 1896, p 9

[2] Schönrock · Ztschr. für Instrum., 16, 243 (1896)

E. DETERMINATION OF THE CONCENTRATION OF SOLUTIO

171. Calculation of the Concentration from the Specific Gravity ε **Percentage Strength.**—The concentration c, by which is und stood the number of grams of active substance in 100 cc. solution, is found by taking the product of the percenta strength p, and the specific gravity d_t, found as explain above.

(I) $$c_t = pd_t.$$

While, now, the percentage strength p is perfectly indepe dent of the temperature, the concentration c varies with We have, in analogy with equation (VII) (§170),

(II) $$c_t = c_{t'} + c_{t'}\gamma_{\frac{t+t'}{2}}(t'-t).$$

As p and d may be determined with great accuracy, it fo lows from (I) that c may be also exactly found. As we hav seen in §166, it is possible, for example, to determine the pe centage strength of a 24 per cent. sugar solution to abo ± three units in the third decimal place. As, further, accor ing to §168, its specific gravity may be found accurately t about ± six units in the fifth decimal place, it follows that th concentration (about 26) may be found for the same tempe ature to within about $^1/_{6000}$ of its amount; that is, to ± 4 units i the third decimal place accurately.

But equation (I) gives the exact concentration only when th specific gravity d is referred to water at 4°. Of course, in th case, we understand by 1 cc. the volume which 1 gram of wate occupies at 4° weighed in vacuo. This cubic centimeter, almos universally employed in scientific work, is usually designate as the true cubic centimeter,[1] and is always understood in wha follows, unless something else is mentioned. This true or prac tical cubic centimeter is, of course, to be distinguished fron the theoretical cubic centimeter; that is, the volume of a cub whose edge is 1 cm. long. From the investigations of Men deléeff and Macé de Lépinay, it follows that 100 practica cubic centimeters = 100.010 theoretical cubic centimeters. If for example, 100 practical cubic centimeters contain 26 gram of substance, then, with reference to theoretical cubic centimeters, $c = 25.9974$; in scientific work calculations are never based on theoretical cubic centimeters.

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[1] As distinguished from the Mohr cubic centimeter.

Concerning the Mohr cubic centimeter, no longer used in science, see §126.

172. **Preparation of Solutions in Measuring Flasks.**—The concentration may also be found directly by dissolving a weighed amount[1] of the active substance in a measuring flask of definite volume. But this method has the disadvantage that the determination of volume in the measuring flask is by no means as accurate as in the pycnometer, and further, that larger volumes of liquid must be brought to a constant temperature, which requires a correspondingly longer time. For exact experiments the method with the pycnometer is decidedly preferable.

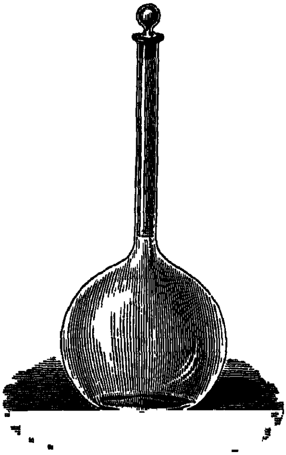

Fig 83

The measuring flasks to be used are illustrated in Fig. 83, and have a volume of 20 to 200 cc., with a neck about 10 mm wide; the circular mark on the neck should be down near the body so as to diminish inequality in the solution as far as possible. Measuring flasks with a long narrow neck divided into tenths of cubic centimeters, and closed with ground glass stoppers, and which have still sufficient mixing space above the upper mark so that solutions with any volume between 100 cc. and 110 cc. may be made, are very practical. Before the solution, made either in the flask itself or in another vessel, is diluted to the mark, a thermometer is dipped in it and the normal temperature (20°) secured by help of a water-bath. Finally, the thermometer is lifted, rinsed off with a little of the solvent, more is filled in to the mark and the whole is well shaken after inserting the glass stopper.

The contents of the measuring flask must be accurately determined by weighing before use. For this purpose, it is f nearly to the mark with air-free water, a thermometer i serted and by warming or cooling in a water-bath it is bro to the normal temperature *t*, for which it is to be used. A withdrawing the thermometer, enough water is added to b the lower edge of the concave liquid surface exactly tange the mark when viewed horizontally. Then, all drops hangin the neck of the flask are removed and the mass *P* of the wa in vacuo, found according to §165 and §166. If the spe gravity of water at the temperature *t* of experiment is *Q* table, §169), then the volume V_t in cubic centimeters, wh the flask contains at $t°$, is given by the equation:

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[1] The weight must, of course, be reduced to vacuo.

$$V_t = \frac{P}{Q} \qquad \text{(III)}$$

It is possible in this manner, with several weighings, to the volume of the flask within about ± 0.03 cc.

When a measuring flask is to be used at any other temp ture t' than the temperature *t* for which it was graduated, cubical expansion of the glass must be taken into considerati If 3β represents this coefficient (in the mean 0.000024), V_t the volume of the flask at the temperature of graduati then this formula may be used in finding the volume at t' ·

$$V_{t'} = V_t + V_t \, 3\beta \, (t' - t). \qquad \text{(IV)}$$

To obtain an idea of the errors connected with the deter nation of concentration of solutions made in a measuring fla we can take as an illustration the preparation of the nor sugar solution commonly employed in saccharimetry. Since 17.5°, 26.003 grams of sugar (true mass) must be dissolved make 100 cc. (§126), the concentration of a correct nor solution is $c_{17.5} = 26.003$. If we now assume that the su is correctly weighed out and that errors in the flask in c junction with inaccuracies in filling to the mark amount only ± 0.02 cc., the concentration is already wrong ∓ 0.0052, an error which is larger than that found in §1 On the other hand, assuming that at the time of preparing t solution the water has a temperature of 18.5° instead of 17 according to (IV) the volume of the measuring flask is longer 100 cc., but 100.0024, and the 26.003 grams of sugar a contained in this. Accordingly the concentration of the pr pared solution is $c_{18\,5} = 26\ 0024$; as further, the coefficient of expansion of a normal sugar solution at 18° is 0.000283, then, according to (II), $c_{17.5} = 26.0098$. In this case, therefore, a temperature difference of 1° in the preparation of the solution makes a difference of 0.007 in the concentration.[1] *It is seen from this how closely the temperature must be controlled when solutions are prepared in the measuring flask.*

F. EFFECT OF THE DIFFERENT ERRORS OF OBSERVATION ON THE SPECIFIC ROTATION

173. **Calculation of Errors.**—Each of the factors entering the formulas $[\alpha] = \frac{100\,\alpha}{l\,p\,d}$ or $\frac{100\,\alpha}{l\,c}$, is attended by a certain error of observation. If we represent by $f(\alpha)$ the error in α, by $F(\alpha)$ the error in $[\alpha]$ caused by $f(\alpha)$, and if $f(l), f(p) \ldots F(l), F(p)$ have the same meanings with reference to l, p, then, since $[\alpha]$ is proportional to α, $l, \ldots$, the following simple relations exist.

$$F(\alpha) = f(\alpha)\,\frac{[\alpha]}{\alpha}, \quad F(l) = -f(l)\,\frac{[\alpha]}{l}$$

$$F(c) = -f(c)\,\frac{[\alpha]}{c}$$

$$F(p) = -f(p)\,\frac{[\alpha]}{p}, \quad F(d) = -f(d)\,\frac{[\alpha]}{d}$$

In the calculation of the errors, F, it is only necessary to use approximate values and two places of figures will be sufficient

To secure a fairly close idea of the influence which each error has on the value of $[\alpha]$, we shall carry through the computation for the case of the determination of the specific rotation of cane-sugar in water where $[\alpha]$ is about 66. Let $\alpha = 35°$, $l = 2$ dm., $p = 24$, $d = 1.1$; these factors may be found with about this degree of accuracy: $f(\alpha) = \pm\ 0\ 004°$, $f(l) = \pm\ 0.0002$ dm., $f(p) = \pm\ 0.003$, $f(d) = \pm\ 0.00006$. From these the following errors are calculated for $[\alpha]$ $F(\alpha) = \pm\ 0.008$, $F(l) = \mp\ 0.007$, $F(p) = \mp\ 0.008$, $F(d) = \mp\ 0\ 004$ As seen, the errors in $[\alpha]$ are of the same order, so that the final accuracy in $[\alpha]$ is about $\pm$ 0.014, or 0 02 per cent.; that is, the specific rotation in this case is found to within about $^1/_{5000}$ of its value. *In all investigations one must take*

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[1] Corresponding to 0 03° Ventzke.

into account, in this manner, the degree of accuracy with w the different measurements may be carried out, in order that estimate of the value of the final result is possible.

The chemist may reply that such great accuracy in specific rotation is not to be reached because of the chem impurity of the substance investigated While this is actua true in very many cases, this very fact should call for more ac rate work in the determination of specific rotation. *It is o after preparations, which have been made or purified by differ methods, have in turn been examined with great accuracy, w the result that differences in the specific rotation are found wh lie quite outside the errors of observation, that it may be sta with positiveness that these differences are due to impurities in material investigated.* At the present time, in the gre majority of cases, and especially in respect to the common and most frequently studied bodies,[1] we are still quite uncerta whether the different values in the specific rotation, found different observers, are due to errors of observation or to i purities in the substances. Along with accidental erro which follow from uncertainties in the observations, there a the systematic errors which are due in the main to the pec liarities in individual instruments, and to these the greate attention must be paid. Considering the delicacy of instruments and methods to-day, certainly no great skill is require to obtain results which agree perfectly with each other aft repeating whole series of observations by one and the sam method, *but the skill of the observer is to be judged rather by h success in eliminating systematic errors by variations in metho and accurate investigation of the apparatus employed.* Bessel' statement cannot be too highly appreciated, that every piec of apparatus must be twice constructed, first by the instrument-maker, then by the observer; which is to say, that before use every measuring instrument must be accurately investigated as to its errors.

For fuller details concerning calculation of errors, see Kohlrausch's "Praktische Physik," 1896, p 1 to 27, or Ostwald' "Physiko-chemische Messungen," 1893, p. 1 to 18 (conside especially page 9).

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[1] See, for example, the constants of rotation of cane-sugar, tartaric acid, alkaloids etc., given in Part VI

PART FIFTH

Practical Applications of Optical Rotation

1. Determination of Cane-Sugar. Saccharimetry

A Determination of Sugar with Instruments having a Circular Graduation

174. By aid of the polaristrobometers described in §98 to §121, the concentration c or the number of grams of sugar in a solution, may be found by the following formula, where we measure the angle of rotation α_D for a layer l decimeters in length

$$c = \frac{100\,\alpha}{l\,[\alpha]}$$

As shown by Table II on page 465, to follow, we can take for the specific rotation of cane-sugar the constant value $[\alpha]_D = + 66.5$, for all concentrations below $c = 30$. This is sufficiently close for practical work, as c may be found from it with accuracy to 0.01 or 0.02. If this number is substituted in the above equation, there follows,

$$c = 1.504\,\frac{\alpha_D}{l}$$

For a 2 dm. tube

$$c = 0.752\,\alpha_D.$$

The percentage amount of pure sugar in a solid saccharine body, of which P grams have been dissolved to make 100 cc., and which is examined in an instrument with circular graduation, is given by the proportion,

$$P : 0.752\,\alpha :: 100 : x,$$

$$x = \frac{75.2\,\alpha_D}{P}.$$

175. If we have to analyze very strong sugar solutions, or if the greatest degree of accuracy is desired, then the change in

the specific rotation $[\alpha]$ with the concentration must be
into consideration. The following formulas are given to
the dependence of the specific rotation of cane-sugar, o
percentage strength p:

I. $[\alpha]^{20}_{D} = 66.386 + 0.015035p - 0.0003986p^2$(Tollens.)[1]

II $[\alpha]^{20}_{D} = 66.438 + 0.010312p - 0.0003545p^2$(Nasini and Villavec

The following table (Table I) contains in columns d a
the specific rotations calculated according to the above form
and corresponding to percentage amounts of sugar (colum
increasing from 5 to 5 per cent

TABLE I

a	b	c	d.	e	f.
			Specific rotation $[\alpha]^{20}_{D}$.		
Per cent amount p	Sp gr $d\ ^{20}/_{4}$ Interpolated from the nearest values of Tollens d	Concentration ($c = p\ d$ according to Tollens) c	Calculated by Formula I (Tollens), referred to p	Calculated by Formula II (Nasini), referred to p	Calculate Formula referred c
5	1.01786	5.0893	66.451	66.480	66 47
10	1.03819	10.3819	66 496	66.506	66.50
15	1 05926	15.8889	66 522	66 513	66.51
20	1 08109	21.6218	66.527	66.502	66.51
25	1.10375	27 5938	66.513	66 474	66.496
30	1.12721	33.8163	66.479	66.428	66 46
35	1.15153	40.3036	66 424	66.365	66 404
40	1.17676	47.0704	66.350	66.283	66 324
45	1.20288	54.1296	66.256	66 184	66 217
50	1.22995	61.4975	66.142	66.067	66 081

The values in columns d and e may be used when the p
centage amount of sugar, p, in 100 parts by weight of a sol
tion is to be found, but the specific gravity must also
known. We find p from

$$p = \frac{100\,\alpha}{l\,d\,[\alpha]}.$$

We proceed in this way. An approximate value for $[\alpha]$
substituted and p calculated; then the exact value of $[\alpha]$

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[1] See Part VI, Constants of Rotation

[2] See next page

taken from the table or is interpolated, and on substitution of this in the formula the exact value of p may be found.

But the case is much more common in which we desire to find, not the percentage amount, but the concentration of a solution. The formula given above,

$$c = \frac{100\,\alpha}{l\,[\alpha]},$$

possesses this advantage that the specific gravity of the sugar solution investigated need not be known, and that at the same time the latter may contain inactive substances also along with the sugar. As up to the present time we have had no formula which presented the specific rotation of cane-sugar as dependent on the concentration, the following new one has been calculated from the observations of Tollens and Nasini.

III $[\alpha]^{20}_D = 66.435 + 0.00870\,c - 0.000235\,c^2$ (holds for $c = 0$ to 65).

The values of $[\alpha]$, according to this formula, are given in column f of the above table opposite the corresponding values from Formulas I and II.

It will be recognized that all the values from Formula III lie within those from the formulas of Tollens and Nasini. As the latter differ from each other only by amounts which correspond to the unavoidable errors of observation, Formula III, for the concentration, possesses a degree of accuracy which satisfies all practical requirements.

The specific rotation of sugar solutions with from 1 to 65 grams of sugar in 100 cc is then given by the following:

TABLE II

c	$[\alpha]^{20}_D$.	Diff for $c = 1$	c	$[\alpha]^{20}_D$.	Diff for $c = 1$
1	+66.443	+0.0075	35	+66.452	−0.0090
5	66.473	+0.0052	40	66.407	−0.0112
10	66.499	+0.0028	45	66.351	−0.0136
15	66.513	+0.0004	50	66.283	−0.0160
20	66.515	−0.0018	55	66.203	−0.0184
25	66.506	−0.0042	60	66.111	−0.0208
30	66.485	−0.0066	65	66.007	

The following example shows that the change in the specific rotation is marked enough to appreciably affect the results of optical analysis with solutions of considerable concentration.

Let a rotation of 83.11° be found with a 2 dm. tube A‹ ingly, the concentration would be 0.752 × 83.11 = **62.5** of sugar in 100 cc But, according to the table, the s rotation of sugar for this concentration is 66.06. The concentration will then be found from the equation:

$$c = \frac{100 \times 83.11}{2 \times 66.06} = \mathbf{62.91} \text{ grams}$$

B. Determination of Cane-Sugar with Application of W Compensation Instruments and the Ventzke Scale.

176. These instruments which have been described in ‹ in §122 to §137 are the only ones practically employed i sugar industry. In the course of time many different direc have been given for the manner of using them, as well the preparation of solutions of different saccharine substa but at the same time experience has shown that in the re of different observers differences are often found, the cau which must lie in the lack of uniformity in methods of cedure. In consequence of this, it has become necessary the side of the sugar chemist, as well as from that of rev administration to establish definite methods, and this has recently done by the Rules of Procedure provided by German Sugar Tax Law of May 27, 1896, appendices A, I and E The provisions in the last are based in part on man vestigations carried out in the laboratory of the Societ Promotion of the German Beet-Sugar Industry, and par larly those of Herzfeld,[1] and partly on decisions reached ir meetings of societies of commercial chemists [2]

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[1] See especially the following Herzfeld Ztschr Rubenzucker-Ind., **40**, 167 (1890), "Die Bestimmung des Zuckergehaltes der Handelswaare ," **41**, 685 (1891), ' des Invertzuckers in Melassen ," **42**, 147 to 259 (1892), "Ueber die zweckmassigst der Werthschatzung des Rohzuckers ," **43**, (1893), "Die Wasserbestimmung im zucker " Also, Hammerschmidt Ztschr Rubenzucker-Ind , **40**, 465 (1890), "V gemeinerung der Clerget'schen Methode " **41**, 157 (1891), "Bestimmung der Sacch mittelst der Inversionsmethode " Besides these, many other papers.

[2] See Ztschr Rübenzucker-Ind , **36**, 6 (1886), "Bericht über die Sitzung der I zucker-Commission in Magdeburg vom 5 Dec , 1885," and page 11 appendix to this 439 (1890), "Rundschreiben vom 6 Juli, 1890, an die Handelschemiker, betr die Be mung der Raffinose und des Invertzuckers ," page 443, "Anleitung zur Bestim des Gehaltes an Raffinose und Invertzucker in den Producten der deutschen R zuckerfabrikation ," page 446, "Arbeitsvorschrift fur die Invertzuckerbestimmu **45**, 73 (1895), Allg Theil, "Bericht uber die Versammlung der Handelschemiker 12 Marz, 1895, in Berlin ," **46**, 180 (1896), Allg Theil, "Sitzung der Commissio Handelschemiker behufs Prufung von Normalquarzplatten zur Controle der charimeter "

177. For the work in hand, it appears most practical to give below an exact reprint of the four appendices of the sugar tax law referred to (in the order, C, A, B, and E).[1]

[Note by Translator.—Although the directions given below apply in some cases to German conditions only, it was thought best to allow them to stand as written, inasmuch as they are suggestive and have been pretty generally followed in the practice of other countries. Permission was given by the author to modify this section at the discretion of the translator, but instead of doing this, attention will be called to the following books and pamphlets where other details may be obtained .

Wiley's "Agricultural Analysis" Vol III. Parts 2 and 3.

Allen's "Commercial Organic Analysis." Vol. I, 3rd ed. p. 243-379

"Methods of Analysis adopted by the Association of Official Agricultural Chemists." 1898 p. 27-40.

"Revised Regulations Governing the Sampling and Classification of Imported Sugar and Molasses. U. S Treasury Department." Document No. 2113.]

Appendix C

DIRECTIONS FOR MAKING THE POLARIZATIONS

Polariscope —In making polarizations for the purpose of revenue assessment, the Ventzke-Soleil color apparatus or a half-shadow saccharimeter only may be employed. For both instruments, one degree of rotation in a 200 mm tube, at 17 5°, corresponds to a strength of 0 26048 gram of sugar in 100 cc of liquid ,[2] a sugar solution which contains 26 048 grams in 100 cc —the so-called normal weight—produces accordingly a rotation of 100°. Therefore, when a solution of a substance is examined in a 200 mm. tube, and it contains 26 048 grams dissolved to make 100 cc , the degrees of the scale indicate the percentage amount of sugar present If only the half of this normal weight is dissolved, the number of degrees read off must be doubled to obtain the correct per cent. of sugar The same is true for those cases in which the examination is made in a 100

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[1] Taken from Ztschr Rubenzucker-Ind , **46**, 410 to 427, and 435 to 439 (1896) The description of all other methods employed in the laboratories of sugar factories may be found in the work of Frühling and Schulz "Anleitung zur Untersuchung der für die Zuckerindustrie in Betracht kommenden Rohmaterialien, Producte, Nebenproducte und Hülfssubstanzen." Braunschweig, Friedr Vieweg & Sohn, 1897 Fifth edition

[2] Mohr cubic centimeters are referred to. See §126 of this book. If flasks are used which are graduated in true cubic centimeters, the normal weight is 25 987 grams instead of 26.048 grams. See §126 and Ztschr. Rubenzucker-Ind., **41**, 514 (1891) and **46**, 180 (1896)

mm. tube. On the other hand, in investigations where the double
weight is examined in a 200 mm. tube, or where the simple
weight is examined in a 400 mm. tube, it is necessary to take h
number of degrees read off

The investigations are to be made as nearly as possible at th
scribed normal temperature, but slight deviations may be neglecte
Proceed as follows in polarizing

Weighing out and Dissolving the Sample, making up to 10
The tare of the weighing receptacle for the sugar, preferably a p
copper foil bent up on two sides, is found on an accurate balanc
then the normal weight of the sugar, 26 048 grams is weighed out
matter of convenience a weight is used for this which is adjusted
normal weight. In case the sugar sample which is to be tested
homogeneous, it is necessary before weighing to break any lumps p
and mix thoroughly by rubbing with a pestle or with the hand.
necessary to make the weighing quickly because, otherwise, esp
in warm rooms, water may be given off during the process, an
would increase the polarization. The sugar weighed out is shaker
the copper foil through a brass funnel into a 100 cc flask; any rem
particles are washed down with about 80 cc of distilled water from a
bottle, having the room temperature, and then the liquid in the fl
gently shaken until all is dissolved, larger lumps being broken
glass rod Any insoluble residue, such as particles of sand, m
recognized as they cannot be crushed by the rod. In withdrawin
rod, the adhering sugar solution is rinsed down with distilled
Then the volume of liquid in the flask is brought exactly to the
mark with distilled water The flask is held in vertical position ar
water added drop by drop until the lower edge of the meniscus
neck of the flask is exactly even with the mark when this is hel
level with the eye. After filling, the neck of the flask is dried with
paper and then the liquid is well mixed by shaking

Clarification.—Sugar solutions, which, after the filtration to
scribed below, are not clear or are so highly colored that they ar
sufficiently transparent in the polarization apparatus, must, before
to the mark, be clarified or decolorized.

When a color instrument is used 10 to 20 drops, or when necessary,
more, of basic lead acetate solution is added from a small pipette or s
wash-bottle, the amount depending on the nature of the sugar an
intensity of the light from the illuminating lamp employed If c
cation cannot be accomplished in this way, the addition of an equa
ume of alum solution follows the lead acetate, or a few cubic centim
of alum solution may be added first, and then a larger volume of the
lead acetate solution than before, until a filtrate is secured which is n
white or yellowish white If the solutions cannot be clarified in this
then basic lead acetate alone is used and the filtrate is mixed wit
smallest amount of extracted blood charcoal (1 to 3 grams at mos

with bone-black dried at 120°. In this case, the polarization must be increased by the amount of the absorption coefficient of the charcoal which must be found when it is purchased

If a half-shadow apparatus is employed, the addition of 3 to 5 cc of a thin alumina cream along with a little basic lead acetate is usually sufficient Only when the sugar solutions are very highly colored is it necessary to employ the same clearing method given for the color instrument It is scarcely necessary to proceed to the application of blood- or bone-charcoal for the half-shadow instruments, since rather dark sugar solutions may be polarized in these.

After clarification, the inside of the neck of the flask is washed down with water from a wash-bottle and the solution is made up to the mark in the manner described Then any drops of water clinging to the inside of the neck are wiped out by aid of filter-paper, and the contents are thoroughly mixed by shaking after closing the neck with the finger

With reference to clarification, the following general remarks hold for both kinds of instruments :

1. The greater the intensity of the light used with the instrument, the less will be the decolorization required by the liquid. Petroleum, gas, incandescent, or electric lamps constructed for the purpose may be used. With half-shadow instruments, it is necessary to purify the light from other than yellow rays by aid of a chromate plate or chromic acid solution furnished with the apparatus With application of incandescent gas light this addition is always necessary
2. When using basic lead acetate for clarification, a large excess must never be added With a little practice, one learns when to stop with the acetate But, if too much basic lead acetate has been added, the excess must be precipitated by addition of alum solution in the manner shown above
3. The action of the clearing solutions is the stronger, the more perfectly the mixture is shaken after filling to the mark

Filtration.—Proceed next to filtration of the liquid, which is done by aid of a paper filter in a glass funnel The funnel is placed over a so-called filtering cylinder which receives the liquid, and during the operation is covered with a glass plate, or watch-glass, to prevent evaporation The funnel and cylinder must be perfectly dry , any moisture present would have the effect of diluting the 100 cc.

It is convenient to have the filter large enough to receive the whole 100 cc of liquid at one time , it is also recommended, unless the paper is very thick, to use a double filter. The first drops which pass through are thrown away, as they are turbid and modified by the moisture of the paper. If what follows is also turbid, it must be returned to the funnel until a clear filtrate runs through. It is absolutely necessary to observe these precautions, because an accurate polarimetric observation can be made only with a clear liquid.

Filling the 200 mm. Tube.—After a clear solution is secured in the manner described above, the tube which is used in the polarimetric mination is filled with the liquid necessary from the filtrate i cylinder

As a rule, a 200 mm tube is employed, but with solutions, whi spite of all efforts at clarification, are still turbid or dark, a 100 mm is preferable.

These observation tubes are made of brass or glass, they are clos both ends by means of round glass plates, so-called cover-glasses cover-glasses are held by means of screw caps, or by a spring cap v is shoved over the tube and is held in place by the spring.

The tubes must be most carefully cleaned and dried. The cleani most easily accomplished by washing with water and then by pushin wads of filter-paper through them by aid of a wooden rod The c glasses must he polished perfectly bright and must not show any in fect places or scratches Avoid warming the tube by the hand when filled. Therefore, hold the tube, which is closed below, by only fingers, and fill it so the liquid meniscus projects above the upper ope then wait a short time to allow any air bubbles to escape and push o cover-glass from one side in a horizontal direction The cover- must be put on so quickly and carefully that no air bubble can under it If it is not satisfactorily done the first time the operation be repeated, after having cleaned and dried the cover-glass and fille the meniscus with a few drops more of liquid. After bringing the c glass in place, the tube is closed with the cap If this is accompli by a screw cap the greatest care must be taken to turn it on only s as is necessary to hold the cover in firm position; if it is pressed too h the cover-glass may become optically active and an incorrect resul found on polarization If the screw has been turned too far, it is sufficient simply to loosen it, but some time must be allowed to before the polarization can be made, since the glass often loses the parted polarizing power but slowly To be perfectly certain, the ob vation should be repeated several times after intervals of ten min until the result shows no further change

Preparation of the Instrument for Observation—After filling tube it should be held up toward the light to see if the field of v appears perfectly round, and if any part of the rubber ring placed u the cap to diminish the pressure on the cover-glass extends over the o ing in the metallic ring If the rubber is found to project in this w new dry tube with a larger ring opening should be taken and filled an The apparatus is then made ready for the observation. It should placed in a room, the windows of which may be darkened as far as p ble by curtains, so that the eye will not be disturbed by outside l during the observation Care should be taken to have the lamp wh furnishes the light for the apparatus in good condition. The lam placed at a distance of 15 to 20 cm from the instrument, and after lig ing it, wait at least a quarter of an hour before beginning the observati Any changes in the character of the flame, as well as a change of dista between the lamp and polariscope, or turning the wick or the flame up or down, or any movement or turning of the lamp, affects the results of the observations.[1]

By moving the telescope at the front end of the instrument it is so adjusted that the hair line, which divides the field of view into two halves, appears clearly defined. The eye should not be held right at the ocular of the telescope, but at a distance of 1 to 3 cm., and during the observation the whole body should be in a perfectly comfortable position, since any unnatural position leads to a strain which disturbs the eye If the apparatus is properly adjusted the field of view is round and sharply defined. One should not be satisfied with a partial fulfilment of these conditions, but should change the position of the instrument, the lamp or the telescope, as necessary, until the desired end is reached.

Zero Point Adjustment.—Then proceed to the determination of the zero point With beginners it is advisable to place a tube filled with water in the instrument, as thereby the field of view is enlarged and the observation made easier

With a color instrument, finding the so-called transition tint precedes the actual zero point adjustment To this end the screw head on the right of the apparatus is turned until, with a little practice, a certain easily recognized light blue or blue violet shade is secured at about the right zero position

The sharp zero point adjustment is made by turning the screw head under the telescope, to and fro, until, at the right point, the two halves of the field of view have the same tint in a color instrument, or are equally dark in a half-shadow instrument

The result of the zero point adjustment is determined in the same manner in both forms of instrument This result is read off on the graduated scale provided with a vernier, by means of an observing telescope, the scale being sharply illuminated by aid of a candle flame On the fixed vernier ten divisions correspond in length with nine divisions on the scale, the zero point of the vernier shows the whole number of degrees, while the vernier divisions serve to determine the tenths to be added. If the zero point of the apparatus is correctly adjusted the point indicating it must coincide with the zero of the vernier If this is not the case the deviation must be noted and afterwards must be used to correct the polarization reading.

One must not be satisfied with a single zero point reading, but five or six readings are made, and the mean of the deviations is calculated If single readings show a variation of more than three-tenths of a division from the mean, they are left out of consideration as incorrect. Between two readings the eye should be allowed to rest twenty to forty seconds.

If a number of analyses are to be made in succession it is not necessary to find the zero point before each one, but it is sufficient if this is done after the lapse of an hour.

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[1] This is not the case if the path of the rays through the instrument is correct, according to §96 of this book. See also §129

Polarization of the Solution.—After the zero point has been foun tube is filled with the sugar solution and placed in the apparatus. The scope is again focused until the dividing line between the fields i tinctly visible and a perfectly round image of the field of view is sec If the field appears dim, even after change in the focus, it is necessa repeat the work from the beginning. But if a clear image is obtaine screw head under the telescope is turned until uniformity in tint cured in a color instrument, or agreement in shade in the half-sh instrument. Then the nearest number of degrees is read off on the and the tenths on the vernier. Five or six single observations are i as before, at intervals of ten to forty seconds, and the mean of these t as the final result of the polarization. If the zero point did not sta exactly the right place, the variation in the reading must be added was toward the left, and must be subtracted if it was shoved to the ri also, in case bone-black was employed in the clarification, a corre must be made as explained above.

Control of the Apparatus.—Every polarizing instrument must be te before its first use, and also afterward, from time to time, especially has been shaken or jarred, to determine its accuracy, and this is don finding the zero point and examining the scale by aid of so-called no quartz plates whose polarization is known. The test may be made by use of 26.048 grams of pure sugar, the solution of which should po ize exactly 100 degrees when the zero point is placed correctly.

Append

DIRECTIONS FOR THE REVENUE OFFICIALS

in testing sugar sirups for invert sugar, and in fixing the quotient sirup containing less than 2 per cent. of invert sugar.

1. Testing Sugar Sirups for Invert Sugar

Exactly 10 grams of the sirup, previously made thin by warming, weighed into a porcelain dish and brought into solution by stirring a addition of 50 cc. of warm water. As a rule, the solution does not quire filtration, even if it appears cloudy. It is poured into an Erlenme flask of about 200 cc. capacity, or into a correspondingly large porcel dish, and then 50 cc. of Fehling solution is added.

The Fehling solution is made by mixing equal volumes of blue vit solution (34.639 grams of crystallized copper sulphate to make 500 c and alkali-Rochelle salt solution (173 grams of crystallized Rochelle in 400 cc., this solution mixed with 100 cc. of a sodium hydroxide so tion which contains 500 grams in a liter). The two liquids, which may obtained from chemical dealers, must be kept separate; of each one, cc. is taken by a special pipette and added to the solution of the su sirup with stirring. If a large number of tests are to be made at one t the two constituents of the Fehling solution may be mixed with ea other in correspondingly large amount, but the use of such a mixtur allowable only within three days, because on longer standing it becon valueless for analysis.

The liquid mixed with Fehling solution is heated in a flask on gauze over a Bunsen burner or a good alcohol lamp, brought to boiling and kept in ebullition two minutes This time of boiling must not be shortened.

Then the lamp is removed and the liquid is allowed to stand at rest a few minutes to permit a precipitate to settle; the flask is held toward the light to see whether or not a blue color remains. If there is still copper in the solution, which is shown by a blue color, the solution contained less than 2 per cent of invert sugar

The color is more easily recognized by holding a sheet of white paper back of the flask and examining it in reflected light

If, after boiling, the liquid appears yellowish green or brownish it is possible that undecomposed copper solution is still present, but masked in color by the yellowish brown color of the sirup In such cases, proceed as follows·

A small filter is made of good thick filter-paper, placed in a glass funnel and moistened with a little water so that it may be pressed against the edge of the funnel The funnel is placed over a test-tube, then, about 10 cc of the boiled liquid is filtered, and to the filtrate about the same volume of acetic acid and one or two drops of an aqueous solution of potassium ferrocyanide are added If an intense red color appears in the filtrate, copper is still in solution and it is so shown that the sirup contains less than 2 per cent of invert sugar

2. Determination of the Quotient for Sugar Sirup Containing Less than 2 Per Cent. of Invert Sugar

The quotient (or coefficient of purity) is that per cent of sugar in the solids of the sirup which may be calculated from the polarization and the specific gravity on the Brix scale

a To Find the Specific Gravity in Brix Degrees.

In a tared beaker, weigh off 200 to 300 grams of the sirup to be tested 100 to 200 cc of warm distilled water is added, the mixture is carefully stirred (to avoid breaking the glass) until the whole is brought into solution, and then the beaker is placed in cold water until the contents have cooled to the room temperature Then the beaker is placed on a balance, and water is carefully added from a wash-bottle until the whole weight of added water is just equal to that of the sirup taken For example, if 251 grams of sirup were taken for testing, then water must be added until the liquid weighs 502 grams After adding the water the liquid is stirred and filled then into the specific gravity cylinder so far that, after immersion of the Brix spindle, it does not reach quite to the upper edge The cylinder must be placed in a vertical position so that the spindle will float freely without touching the sides. The spindle is immersed slowly, and care must be taken not to moisten that part of the stem which remains above the liquid after the spindle has come to rest When this condition is reached, the saccharometer degrees are read off at the point where the liquid meniscus cuts the stem

The number of degrees read off on the spindle holds for the ı temperature of 17.5° C. If the liquid does not happen to hav normal temperature, the degrees read off must be corrected by aid following table, after the true temperature is found by means of ı mometer attached to the body of the spindle

After the correction, the Brix degrees are to be rounded off in t by considering five or more hundredths as a full tenth, and s fractions neglected.

The number of degrees read off are to be multiplied by 2, becau liquid employed in the test had been diluted with an equal wei water.

TABLE FOR THE CORRECTION OF BRIX DEGREES FOR TEMPERA DIFFERENT FROM THE NORMAL TEMPERATURE (17.5° C.)

At a centigrade temperature of	and at							
	25	30	35	40	50	60	70	
	Brix degrees							
	There must be taken from the saccharometer readings Degrees							
0°	0.72	0.82	0.92	0.98	1.11	1.22	1.25	1
5	0.59	0.65	0.72	0.75	0.80	0.88	0.91	0
10	0.39	0.42	0.45	0.48	0.50	0.54	0.58	0
11	0.34	0.36	0.39	0.41	0.43	0.47	0.50	0
12	0.29	0.31	0.33	0.34	0.36	0.40	0.42	0
13	0.24	0.26	0.27	0.28	0.29	0.33	0.35	0
14	0.19	0.21	0.22	0.22	0.23	0.26	0.28	0
15	0.15	0.16	0.17	0.16	0.17	0.19	0.21	0
16	0.10	0.11	0.12	0.12	0.12	0.14	0.16	0
17	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0
	There must be added to the saccharometer readings							
18	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.
19	0.10	0.10	0.10	0.10	0.10	0.10	0.08	0
20	0.18	0.18	0.18	0.19	0.19	0.18	0.15	0.
21	0.25	0.25	0.25	0.26	0.26	0.25	0.22	0.
22	0.32	0.32	0.32	0.33	0.34	0.32	0.29	0
23	0.39	0.39	0.39	0.40	0.42	0.39	0.36	0.
24	0.46	0.46	0.47	0.47	0.50	0.46	0.43	0.
25	0.53	0.54	0.55	0.55	0.58	0.54	0.51	0
26	0.60	0.61	0.62	0.62	0.66	0.62	0.58	0.
27	0.68	0.68	0.69	0.70	0.74	0.70	0.65	0.
28	0.76	0.76	0.78	0.78	0.82	0.78	0.72	0.
29	0.84	0.84	0.86	0.86	0.90	0.86	0.80	0.
30	0.92	0.92	0.94	0.94	0.98	0.94	0.88	0

b. Polarization

In the polarization of sugar sirups, because of the dark color, the directions given in Appendix C for determination must be modified in these respects

Only the half weight, 13.024 grams, is taken in testing sugar sirup. This is weighed into a porcelain dish and treated with 40 to 50 cc of lukewarm distilled water, and stirred with a glass rod until it has dissolved completely. Then the liquid is washed into the flask and before filling to the mark is clarified

For the clarification about 5 cc. of basic lead acetate solution is run first into the flask. If after the precipitate has settled, which follows in a few minutes, the liquid is still too dark the addition of the lead acetate is continued until the desired brightness is secured As much as 12 cc. of the basic acetate is often required for this. But it must be observed that the basic acetate must be added in sufficient, but not in excessive, quantity; each new drop added must produce a precipitate in the liquid

If it is found that the latter cannot be sufficiently clarified by the addition of basic lead acetate to be polarized in the 200 mm tube, an effort should be made to polarize it in the 100 mm tube If this is likewise impossible a new sample should be prepared, which is treated with about 10 cc of an alum or tannic acid solution before the addition of the basic lead acetate, these solutions produce heavy precipitates with basic lead acetate, which have a clarifying effect and permit the use of larger quantities of the lead solution

After the polarization is made the number of degrees read off must be multiplied by 2, since only the half-normal weight was taken for the test If a 100 mm tube was employed in place of the 200 mm tube the number of degrees read off must be multiplied by 4.

c Calculation of the Quotient

If the observed number of Brix degrees be designated by B, and the degree of polarization by P, then the quotient is calculated by the formula, $Q = \frac{100\ P}{B}$. In stating the final result smaller fractions than full tenths are omitted.

Illustration of the Determination of the Quotient—200 grams of a sugar sirup are diluted with 200 grams of water The Brix spindle indicates 35.2° at a temperature of 21° C; from the above table 0 25 must be added; this gives then 35.45°, or rounded off 35 5°, and after multiplying by 2, 71° Brix The polarization of the half-normal weight in a 200 mm. tube gave 25 2°; the true polarization is then $25.2 \times 2 = 50.4°$ The quotient calculated is therefore $\frac{100 \times 50.4}{71} = 70\ 9$.

Final Provision

Revision reports must contain the following data · the result of the test for invert sugar, the number of degrees read off on the areometer, the temperature of the solution, the calculated areometer degrees f undiluted sirup, the polarization for the whole normal weight a quotient.

Appe

DIRECTIONS FOR CHEMISTS

I In determining the quotient for sirups containing 2 per cent. or of invert sugar, and the quotient of sirups to be examined for nose,

also,

II. In determining the amount of sugar in crystal sugar supposed t tain raffinose.

I. The Quotient for Sirups

According to the regulations provided by the sugar tax law the c mination of the quotient for a sirup shall be left to a chemist when :

a There is no official properly qualified to determine the quotie the point of declaration or at the office to which the sample is

b The sirup contains 2 per cent or more of invert sugar;

c. The one presenting the sample asks for the calculation of the tient from the amount of pure sugar chemically determined.

When samples are sent from the revenue office to a chemist he mu informed as to which one of the above grounds the investigation is c for, and besides in cases coming under *c*, whether or not the applica of the raffinose formula is allowable, according to the directions o section 5 of the last part of the Rules of Procedure, where 2 or n per cent. of invert sugar may be present

In cases under *a* the chemist must proceed as in Appendix A of Rules of Procedure, but with the condition that the Brix degrees ar be found as given in the following section 1

In cases under *b* the quotient must be found as explained in the foll ing section 1

In cases under *c*, as far as the use of the raffinose formula is allowa the method of section 2 below must be followed, otherwise the metho according to the provisions of section 1 If the propriety of using raffinose formula depends on whether or not the sirup contains less t 2 per cent of invert sugar, then the sirup must be tested according to method of section 1 in Appendix A

1 Determination of the Quotient in Sirups Containing 2 Per Cent More of Invert Sugar

In the investigation of sirups containing 2 per cent or more of inv sugar the Brix degrees must be calculated from the specific gravity of undiluted sirup found by aid of a pycnometer

If a quotient of 70 or more is found from the number of Brix degr and the direct polarization to be always made in connection, then a further investigation is to be dropped, as this would only lead to an crease of the quotient.

But if a quotient below 70 is found in this preliminary test then the exact determination of the amount of sugar is called for. In this it is not the saccharose alone which is to be calculated as sugar, as in factory work, but the invert sugar present, which is calculated to cane-sugar by the subtraction of $^1/_{20}$, is to be added to the latter and the sum then taken as the basis of the calculation.

In sirups the invert sugar is often inactive, but it may have the normal left rotation and, therefore, make the polarization of the cane-sugar present appear too low For this reason it is not permissible in the examination of sirups, to proceed as was suggested by Meissl for solid sugar-cane sugars, to multiply the invert sugar by 0.34, and to add the product obtained to the polarization If one should proceed in this way, the sugar content of a sirup would, in many cases, be made to appear too high But the possibility must always be kept in mind that, in consequence of the left-hand rotation of invert sugar, in presence of much of the latter the cane-sugar content will be found much too low In consideration of these conditions, it appears in general that the calculation of the total sugar from the polarization and the invert sugar found is allowable only in those cases where the amount of invert sugar does not exceed a certain limit. As an illustration, in presence of 6 per cent of invert sugar the polarization of beet-sugar could be $6 \times 0\ 34 = 2\ 04$ per cent. too low. It is then advisable, in general, to abandon the optical method for sugar determination in sirups and to apply a gravimetric estimation for which a method that can be quickly carried out is given below under *a*

But an exception must be made when starch sugar is added to the sirup As we are unable to determine accurately the amount of starch sugar present, and as, in addition, the reducing power of this sugar, which in the commercial product corresponds to a content of 40 to 60 per cent of dextrose, remains practically constant under the conditions which are applied in the inversion of sirup for carrying out the gravimetric method, it follows that in cases where this sugar is added, the gravimetric method for determination of the total sugar content, or the quotient, can no longer be applied. It would lead, on the contrary, to gross errors, and sirups with a quotient above 70, with a certain amount of starch sugar added, would be made to appear, when tested in this way, as having a quotient below 70 With starch sugar present, the left-hand rotation of the invert sugar no longer affects the polarization as in the case of unmixed sirup, because the starch sugar has a much greater right-hand rotating power than the other kinds of sugars which may be there To guard against mistakes which are easily possible with the mixing of starch sugar and sirups having a quotient over 70, the total sugar content, in all cases when starch sugar is added, must be calculated from the polarization and the invert sugar determined directly, as explained below, under *b*

Every sirup which contains 2 per cent or more of invert sugar must, therefore, be tested to find whether or not it contains starch sugar.

In sugar factories starch sirup is seldom added to cane-sugar s
As a rule, molasses, which are to be sent to distilleries or to factori
the extraction of sugar, do not contain starch sugar, because such
could be worked only with difficulty in these places. If the ch
making the tests has reason to believe from his knowledge of the
or destination of the sugar sirup in question, and after proper cons
tion, can assume with sufficient certainty that it does not contain
sugar, then he may omit the chemical tests which would be calle
But, in other cases, the chemical examination for starch sugar mu
made in the following manner:

The half normal weight is dissolved in the 100 cc. flask in 75
water, and inverted at 67° to 70° C by addition of 5 cc of hydrocl
acid of 1.19 specific gravity Then the flask is filled to 100 cc, an
solution is decolorized by addition of ½ to 1 gram of blood- or bone-
coal which has been washed with hydrochloric acid, or, with dark si
with even 2 or 3 grams, added directly to the flask in dry conditio
blood-charcoal is used, its absorption factor for invert sugar must b
termined, as it is not the same for all kinds, and a corresponding
rection made on the polarimeter reading. Unadulterated sirups, as f
by experience, show often less than the normal left-hand rotation, v
at 20° is 0.327 of the original right-hand rotation, but the amou
always at least the fifth part of the original Therefore, only such s
shall be considered as mixed with starch sugar whose left-hand rot
after inversion is less than one-fifth of the right rotation before inve
For example, a sirup of 55° polarization which, after inversion, sh
rotation of less than —11°, or even a right-hand rotation, must be
sidered as mixed with starch sugar

a. *Sirups free from starch sugar*

In sirups free from starch sugar the determination of total sugar
be made in a single operation.

The half-normal weight (13.024 grams) is taken and dissolved in
cc. flask in 75 cc. of water, 5 cc. of hydrochloric acid of 1.19 sp
gravity is added, and the whole is warmed to 67° or 70° in a water-
The flask is kept five minutes longer at this temperature of 67° t
and is frequently shaken. As the heating requires two and one
to five minutes, the whole operation will consume seven and one-h
ten minutes, in any event it should be completed in ten minutes.
flask is filled to the mark and 50 cc of the 100 cc is then diluted
liter, and 25 cc. of this dilute solution (corresponding to 0.1628 gra
substance) is taken in an Erlenmeyer flask and neutralized by the
tion of 25 cc of a sodium carbonate solution containing 1.7 grams o
anhydrous salt to the liter. Then 50 cc of Fehling's solution is a
and the solution is heated to the boiling-point in the same manner as i
invert sugar determination, and then kept three minutes in ebulli
The liquid should be heated as quickly as possible by means of a
triple burner, using wire gauze and sheet asbestos with a ring cut o

it, and should require three and one-half to four minutes; when the liquid begins to boil rapidly a single burner is exchanged for the triple burner When the boiling is complete the liquid in the flask is diluted with an equal volume of air-free distilled water and the process is conducted in general as in the determination of invert sugar The tables found in the literature cannot be used in the calculation of the result because they do not obtain for invert sugar, but only for dextrose, or for mixtures of invert sugar and saccharose ; the cane-sugar content of the sirup corresponding to the copper obtained must be found by use of the following table only, which gives it directly in per cent The calculation of invert sugar into cane-sugar is then avoided by use of the table

TABLE FOR THE CALCULATION OF CANE-SUGAR IN PER CENT , CORRESPONDING TO INVERT SUGAR PRESENT, FROM THE AMOUNT OF COPPER WEIGHED, AFTER THREE MINUTES' BOILING, WITH 0.1628 GRAM OF SUBSTANCE TAKEN

Copper mg	Cane-sugar Per cent.	Copper mg	Cane-sugar Per cent	Copper mg	Cane-sugar Per cent	Copper mg	Cane-sugar Per cent
79	24 57	106	32 76	133	41 04	160	49 50
80	24 87	107	33 06	134	41 35	161	49 82
81	25.17	108	33 36	135	41 66	162	50 13
82	25.47	109	33 67	136	41 98	163	50 45
83	25 78	110	33 97	137	42 29	164	50 76
84	26.08	111	34 27	138	42 60	165	51 08
85	26 38	112	34 58	139	42 91	166	51 40
86	26 68	113	34 88	140	43 22	167	51 72
87	26 98	114	35 19	141	43 53	168	52 04
88	27 29	115	35 49	142	43 85	169	52 35
89	27 59	116	35 80	143	44 16	170	52 67
90	27 89	117	36 10	144	44 48	171	52 99
91	28 19	118	36 41	145	44 70	172	53 31
92	28 50	119	36 71	146	45 10	173	53 63
93	28 80	120	37 01	147	45 42	174	53 95
94	29 10	121	37 32	148	45 73	175	54 27
95	29 40	122	37 63	149	46 05	176	54 59
96	29 71	123	37 94	150	46 36	177	54 91
97	30 02	124	38.25	151	46 68	178	55 23
98	30 32	125	38.56	152	46 99	179	55 55
99	30 63	126	38 87	153	47 30	180	55 87
100	30 93	127	39 18	154	47.62	181	56 19
101	31 24	128	39 49	155	47 93	182	56 51
102	31 54	129	39 80	156	48 25	183	56 83
103	31 85	130	40 11	157	48 56	184	57 15
104	32 15	131	40 42	158	48 88	185	57 47
105	32 45	132	40 73	159	49.19	186	57 79

Copper mg	Cane-sugar Per cent	Copper mg	Cane-sugar Per cent	Copper mg	Cane-sugar Per cent	Copper mg	Pe
187	58.11	207	64.58	227	71.19	247	7
188	58.43	208	64.91	228	71.53	248	7
189	58.75	209	65.23	229	71.86	249	7
190	59.07	210	65.56	230	72.19	250	7
191	59.39	211	65.89	231	72.52	251	7
192	59.72	212	66.22	232	72.85	252	7
193	60.04	213	66.55	233	73.18	253	7
194	60.36	214	66.88	234	73.51	254	8
195	60.69	215	67.21	235	73.85	255	8
196	61.01	216	67.55	236	74.18	256	8
197	61.33	217	67.88	237	74.51	257	81
198	61.65	218	68.21	238	74.84	258	81
199	61.98	219	68.54	239	75.17	259	81
200	62.30	220	68.87	240	75.50	260	82
201	62.63	221	69.20	241	75.83	261	82
202	62.95	222	69.53	242	76.17	262	82
203	63.28	223	69.87	243	76.51	263	83
204	63.60	224	70.20	244	76.84	264	83
205	63.93	225	70.53	245	77.18	265	83
206	64.26	226	70.86	246	77.51	266	84

In the calculation of the quotient, fractions below whole tenth. neglected

Example. 25 cc. of the inverted sugar sirup = 0.1628 gram of stance, gave on reduction 171 mg. of copper; this corresponds to or rounded off 52.9 per cent. of sugar. Assuming that the sirup sh 75.6 Brix, its quotient is 69.97, or rounded, 69.9.

b. Sirups containing starch sugar

With sirups containing starch sugar in order to obtain the total s content, the plan must be adopted, as mentioned above, of adding t polarization the invert sugar, which is to be calculated from the redu action of the sirup on Fehling's solution

In the determination of the invert sugar in this case, a prelimi test must be made to learn how much substance may be weighed ou the Fehling solution would not be sufficient for the 10 grams usu taken. This is most conveniently done by dissolving 10 grams of siru make 100 cc, and adding different amounts to several portion Fehling's solution of 5 cc each in as many test-tubes, to one 8 cc another 6 cc, to another 4 cc., and to the last 2 cc On boiling now first test-tube which is not decolorized shows the amount to be taken. for example, reduction is not complete in the tube with 6 cc. of the s tion, then 6 grams is the amount of sirup to be weighed out for analysis The right amount of substance is dissolved in 50 cc. of water, mixed with 50 cc of Fehling's solution without previous clarification with lead acetate, boiled two minutes and then treated in the usual manner for the determination of invert sugar in solid sugar The amount of invert sugar is calculated as follows

Let

Pol. = the polarization of the substance,

p = the amount of substance taken for determination of invert sugar, which yields Cu grams of copper

The amount of invert sugar may be taken approximately as $\frac{Cu}{2}$, and may be represented by A We find then from the proportion,

$$\left(A + \frac{p \times Pol.}{100}\right) : A :: 100 : B,$$

for B the amount of invert sugar which is present in 100 parts of cane-sugar + invert sugar

The percentage amount of invert sugar in the substance is given by the formula

$$\frac{Cu}{p} \times F = \text{per cent. of invert sugar},$$

in which p is the amount of substance taken, and F a factor from the table below

In this table the columns and lines are used, the designations of which come the nearest to the values found for A and B, at the intersecting point, the factor F is given

TABLE OF FACTORS TO BE TAKEN FOR THE CALCULATION OF INVERT SUGAR IN PRESENCE OF CANE SUGAR

Invert sugar in 100 parts of total sugar = B	Milligrams of invert sugar = A						
	200	175	150	125	100	75	50
100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

Example Assume that the polarization of the sirup is 86 4, an for 3 256 grams of substance taken (p), the amount of copper found is 0.290, then

$$\left(A + \frac{p \times Pol}{100}\right) : A = \left(0.145 + \frac{3\ 256 \times 86\ 4}{100}\right) : 0.145 =$$

$$2.958 \quad 0\ 145 = 100$$

therefore, $B = 4\ 9$

The nearest value in the table to $A = 0\ 145$ is 150 mg, the num is the nearest to 4.9, the invert sugar in 100 parts of total sugar, a point of intersection of the line 5 with the column headed 150 m find the factor 51.2. If this is substituted in the formula $\frac{\text{Cu}}{p} \times F$ w tain $\frac{0\ 290}{3\ 256} \times 51.2 = 4\ 56$ per cent of invert sugar. Then the i sugar is calculated to cane-sugar by subtraction of $^1/_{20}$, and the resul tained ($4\ 56 - 0\ 23 = 4.33$) added to that for the polarization. F the sum and the Brix degrees the quotient is found in the usual way

2. *Determination of the Quotient in Sirups to be Examined for Raffinose*

After the value in Brix degrees for the sirup in question has been f by the method of section I, the sugar content in the same is found the direct polarization (P), and the polarization at 20°, or at a tem ture very close to this and properly corrected, after inversion (I), b of the following formula :

$$S\ (\text{Sugar}) = \frac{0\ 5124\,P - I}{0\ 839}$$

If the amount of raffinose is to be found in addition, this formu used

$$R\ (\text{Raffinose}) = \frac{P - S}{1\ 852}.$$

The inversion is to be made in the manner described in sectio under *a*.

Example For a sirup showing 85 6° Brix, 76.6° direct polarization — 3.0° polarization after inversion (for the whole normal weight), amount of sugar is found as

$$\frac{0\ 5124 \times 76\ 6 + 3}{0\ 839} = 50.4 \text{ per cent.,}$$

and the quotient is 58.8.

II. Determination of the Amount of Saccharose in Crystal Sugar posed to Contain Raffinose

The determination of the saccharose content of crystal sugar con ing raffinose is made as for sirups containing raffinose, according to directions in I, 2

Only such sugars shall be considered as containing raffinose in w the difference between the saccharose content by direct polarization that found by application of the raffinose formula is more than 1 per cent. for sugars of class *a*, or more than 0.6 per cent. for sugars of classes *b* and *c*, because smaller differences may be found in raffinose free sugars at times, and possibly may be results of errors of observation.

With differences of 1 per cent or 0.6 per cent or less, in the two classes, the result of the direct polarization is to be taken then as showing the real saccharose content of the sugar tested If the polarization is below 90, a further test is unnecessary

In the statement of the final result, fractions below whole tenths are to be dropped. For example, a sugar content of 97 19 is to be rounded off to 97 1.

Final Provision

A written certificate must be made out for each investigation and filed with the office sending the sample in question. Besides an accurate description of the sample this certificate must contain

I. In determining the quotient of sirups ·

1 In the cases described under *a* at the beginning:
the specific gravity, the Brix degrees calculated from this, the direct polarization, and the quotient calculated.

2 In the cases given under *b* .
the result of the test for invert sugar, the specific gravity, the Brix degrees calculated from this, the direct polarization; further, in case a quotient below 70 is found from these data, either a statement of why a test has not been made for starch sugar, or the result of such a test with figures for the polarization found after inversion , further, with reference to sirups free from starch sugar the amount of copper and the calculated sugar content, and for sirups containing starch sugar the amount of copper found, the invert sugar content corresponding to this, the total sugar content (polarization + invert sugar), and finally the calculated quotient.

3 In the cases falling under *c* above
the result of the test for invert sugar, as far as this is necessary, and then, in case the application of the raffinose formula is permissible, the specific gravity, the Brix degrees calculated from this, the direct polarization, the polarization after inversion, the sugar content calculated from these data by aid of the raffinose formula, and the quotient; otherwise, the data given under 2 above

II. In determining the saccharose content of crystal sugar supposed to contain raffinose:
in case the polarization falls below 90, this only, but otherwise, in addition the polarization after inversion, the sugar content calculated by the raffinose formula, and then the resultant saccharose in per cent as required by the regulations

Appe

DIRECTIONS

for finding the amount of sugar in saccharine products

According to §3 of the rules for carrying out the provisions of the sugar tax law, a rebate of the sugar tax for saccharine manufac products, except in the case of caramels containing starch sugar, c allowed only when they are made without the use of honey or s sugar While the fact of not using honey may be established b factory control and the factory production books, the absence of s sugar is to be determined by chemical tests of the products of the fa These investigations are to be made according to the directions in se 1 of Appendix C of the Rules of Procedure, but with this provision in saccharine factory products the presence of starch sugar is to sumed when the left-hand rotation after inversion of the solution is or less, for every 100 parts found in the direct polarization

The saccharose content of starch sugar-free saccharine factory ucts is to be established by different means, according as they co less than 2 per cent , or 2 per cent or more of invert sugar In c quence, the test of the product for invert sugar is to be made acco to section 1, of Appendix B, but with the variation that the sugar tion to be boiled with the Fehling solution shall correspond, not grams of substance, but to 10 per cent polarization.

Of saccharine products which contain less than 2 per cent. of i sugar, the saccharose content will be found according to the Cl method, in which the inversion is to be made exactly as given i directions of section 1 under *a* in Appendix C, and from the sum o two polarizations (before and after inversion) the saccharose conten be found by the formula

$$S = \frac{100\,s}{142.66 - \tfrac{1}{2}\,t},$$

in which S is the amount of sugar, s the sum of the two polariza for the normal weight, and t the temperature at which the polariza were made The constant (C) 142 66 assumes the use of the hal mal weight (13 024 grams) of sugar in the observation, and is to l placed by different numbers corresponding to the amount of subs taken for inversion These numbers are given by the following tab

For grams sugar in 100 c c	For C to be taken	For grams sugar in 100 cc	For C to be taken
1	141.85	11	142 52
2	141.91	12	142 59
3	141 98	13	142.66
4	142 05	14	142 73
5	142 12	15	142 79
6	142 18	16	142 86
7	142 25	17	142.93
8	142 32	18	143 00
9	142 39	19	143.07
10	142 46	20	143 13

If there is found, for example, a direct polarization of + 30 in a 200 mm. tube for a solution of the normal weight dissolved to 200 cc., the calculated direct rotation of the inverted solution containing 75 cc. of the original must be + 22.5. As 100 polarization corresponds to 26.048 grams of substance, 5.86 grams, or rounded off, 6 grams of substance would correspond to the + 22.5°; according to the table, then, the constant 142.18 is to be applied. Assuming then, that a left-hand rotation of — 7.1° is observed at 20°, this corresponds for the half normal weight to $\frac{-7.1 \times 100}{75} = -9.47°$, and for the whole normal weight to — 18.94°. As the direct polarization for the whole normal weight is + 60, the sugar content is calculated as $100 \times \frac{60 + 18.94}{142.18 - 10} = 59.72$ or, rounded, 59.7 per cent., lower fractions than whole tenths being disregarded.

The sugar content of such products as contain 2 per cent or more of invert sugar is to be determined by the copper method given in section 1 of Appendix C of the Rules of Procedure. A portion of the sugar solution is inverted as there explained and the amount of substance to be employed determined as in the case of finding the invert sugar in products containing starch sugar, and then the properly made solution is boiled three minutes with Fehling's solution. The amount of saccharose corresponding to the copper found is given in the following table

TABLE FOR THE CALCULATION OF CANE SUGAR CORRESPONDING TO INVERT SUGAR FROM AMOUNT OF REDUCED COPPER AFTER THREE MINUTES' BOILING

Copper mg	Cane-sugar mg	Copper mg	Cane-sugar mg	Copper mg	Cane-sugar mg	Copper mg	Cane-sugar mg
79	40.0	96	48.3	113	56.8	130	65.3
80	40.5	97	48.8	114	57.3	131	65.8
81	41.0	98	49.3	115	57.8	132	66.3
82	41.5	99	49.8	116	58.3	133	66.8
83	42.0	100	50.3	117	58.8	134	67.3
84	42.5	101	50.8	118	59.3	135	67.8
85	42.9	102	51.3	119	59.8	136	68.3
86	43.4	103	51.8	120	60.2	137	68.8
87	43.9	104	52.3	121	60.7	138	69.4
88	44.4	105	52.8	122	61.2	139	69.9
89	44.9	106	53.3	123	61.7	140	70.4
90	45.4	107	53.8	124	62.2	141	70.9
91	45.9	108	54.3	125	62.8	142	71.4
92	46.4	109	54.8	126	63.3	143	71.9
93	46.8	110	55.3	127	63.8	144	72.4
94	47.3	111	55.8	128	64.3	145	72.9
95	47.8	112	56.3	129	64.8	146	73.4

Copper mg	Cane-sugar mg	Copper mg.	Cane-sugar mg	Copper mg.	Cane-sugar mg.	Copper mg.	C s
147	73.9	176	88.9	205	104.1	234	1
148	74.5	177	89.4	206	104.6	235	12
149	75.0	178	89.9	207	105.2	236	12
150	75.5	179	90.4	208	105.7	237	12
151	76.0	180	91.0	209	106.2	238	12
152	76.5	181	91.5	210	106.7	239	12
153	77.0	182	92.0	211	107.3	240	12
154	77.5	183	92.5	212	107.8	241	12
155	78.0	184	93.1	213	108.4	242	12
156	78.5	185	93.6	214	108.9	243	12
157	79.0	186	94.1	215	109.4	244	12
158	79.6	187	94.6	216	109.9	245	12
159	80.1	188	95.1	217	110.5	246	12
160	80.6	189	95.7	218	111.1	247	12
161	81.1	190	96.2	219	111.6	248	127
162	81.6	191	96.7	220	112.2	249	127
163	82.1	192	97.2	221	112.7	250	128
164	82.6	193	97.7	222	113.2	251	128
165	83.2	194	98.3	223	113.7	252	129
166	83.7	195	98.8	224	114.3	253	130
167	84.2	196	99.3	225	114.8	254	130
168	84.7	197	99.8	226	115.4	255	131
169	85.2	198	100.4	227	115.9	256	131.
170	85.7	199	100.9	228	116.4	257	132.
171	86.3	200	101.4	229	117.0	258	132
172	86.8	201	101.9	230	117.5	259	133.
173	87.3	202	102.5	231	118.1	260	133.
174	87.8	203	103.1	232	118.6		
175	88.3	204	103.6	233	119.2		

The percentage amount of saccharose is calculated from this, and t the total sugar content is expressed as saccharose and given in term per cent. of the substance

With reference to the preparation of solutions of the substance it n be remarked that, as in the case of digestion methods of beet testing is in general not allowable to fill up a flask with the solid substa (chocolates, etc.) and water to the mark, because the error caused by insoluble parts of the solid would be too great. As a rule, therefore, t solution is to be made up to a definite volume only after filtration a washing out of the residue.

With reference to the investigation of saccharine products, on whi rebate is allowable, the following details may be pointed out:

A. Chocolates

It is convenient to moisten the normal weight with alcohol to facilitate the subsequent wetting with water, and then to add about 30 cc. of water and warm ten to fifteen minutes on the water-bath. The liquid is next filtered hot, and may run through turbid without harm ; the residue is washed with hot water. After treatment with about 10 cc. of basic lead acetate the filtrate is allowed to stand a quarter of an hour, then clarified with alum and a few drops of alumina cream, and finally made up to a proper volume, about 200 cc.

B. Confectioner's Wares

a. *Caramels* (*bonbons*, *boltjes*) *with exception of gum drops*, *which are not rebatable*

With regard to such caramels as are declared by the manufacturer to contain starch sugar, it must be determined by tests that they show at least 80° of + rotation and 50 per cent of saccharose by the Clerget process Otherwise they must be considered as not entitled to rebate

Caramels which are declared as free from starch sugar, must be tested for this If no starch sugar is found the further investigation is made as with white sugar candies.

b *Dragées* (*sugar-coated seeds and nuts with addition of flour*)

Dragées are extracted as are chocolates They nearly always contain invert sugar.

c. *White sugar candies* (*sugar with addition of ethereal oils or coloring-matter*)

The solid residue may be neglected The normal weight is, therefore, filled directly into a 100 cc flask, water added to the mark after solution, and the filtration performed afterwards.

d *Porous products* (*mixtures of sugar with some binding substance as white of egg*, *with addition of a flavor or remedial agent*)

The usually very small amount of binding material (white of egg, gelatin, gum arabic, tragacanth or glue) is to be removed by basic lead acetate or alumina

The santonin lozenges, which are classed among the porous products, contain sodium santoninate. The addition of basic lead acetate is necessary to remove the santoninic acid

e *Dessert bonbons* (*creams*, *etc* , *made of sugar and enclosed fruits or marmalade*, *etc.*)

The sample is dissolved in water. If but little residue remains it may be made up to the mark directly , otherwise it is necessary to filter first.

f *Marchpane mass and marchpane cakes* (*sugar with crushed almonds*)

The material is conveniently rubbed up with cold water in a porcelain dish and clarified before filtration with much alumina cream. As a rule marchpane is free from invert sugar.

g. Cakes and similar bakers' wares

The sugar is extracted with alcohol of 85 to 90 per cent. Aft oration of the alcohol the filtrate is tested.

h. Sugar-coated tropical or native fruits, glacé or candied ; fru served in sugar solutions (marmalades, pastes, compotes, jel

If the material is solid, special pains must be taken in the prej of an averge sample of homogeneous composition ; as for exam warming and stirring. The sugar is extracted as for *g* above. As invert sugar is present

C. Alcoholic Liquors Containing Sugar

The alcohol does not interfere with the direct polarization , but be evaporated before the inversion polarization

D. Liquid Refined Sugar

Liquid refined sugar contains invert sugar as a rule The test limited to determining that there is a total sugar content of at 1 per cent

Final Provision

A written certificate for each investigation must be handed to th which submitted the sample, and this must contain, besides ai description of the sample, data on the methods and results of tł carried out, and the percentage amount of sugar calculated from tl

II. Determination of Milk-Sugar

178. The specific rotation of crystallized milk-s $C_{12}H_{22}O_{11} + H_2O$, was found by Schmoeger[1] for solution taining from 0 to 36 per cent. to be, at 20°,

$$[\alpha]_D^{20} = 52\ 53 \text{ } \textit{constant}$$

Exactly the same value was found by Parcus and To at 20° for solutions having a concentration of 4.8 to 7.1 g in 100 cc. Schmoeger found also that in the neighborho 20° the above value of the specific rotation is decreased c for each degree of increase in temperature

As already shown in §72, crystallized milk-sugar exh birotation immediately after solution which, however, ma rapidly changed to the constant rotation by heating to 1 On the other hand, the sugar dehydrated at 100° exhi after solution in cold water, at the outset a lower rotation 1 the normal. This is easily changed also to the normal rota by heating.

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[1] Ber d chem Ges , 13, 1922 (1880)

[2] Parcus and Tollens Ann Chem (Liebig), 257, 160 (1890)

For the determination of milk-sugar with instruments graduated in angular degrees we have

$$[\alpha]_D^{20} = \frac{100\,\alpha}{l\,c} = 52.53;$$

therefore

$$c = 1.9037\,\frac{\alpha}{l},$$

and by use of a 200 mm. tube, with sodium light, at 20°,

$$c = 0.9518\,\alpha,$$

or with the use of a tube 190.37 mm. in length,

$$c = \alpha.$$

If the problem is to test a substance as to its content of milk-sugar in an instrument with the Ventzke scale, it is best to dissolve that weight in a 100 cc flask, which, if it were pure milk-sugar, would polarize 100°. This weight is found from the proportion

$$x : 26.048 :: 66.50 : 52.72^{1}$$

$$x = 32.856.$$

By taking 32.856 grams of substance, each degree would then correspond to 1 per cent. of milk-sugar. If a solution is to be examined and it is required to find the concentration of the milk-sugar in it, it is to be observed that a polarization of 1° V. corresponds to a concentration of 0.32856 gram of milk-sugar in 100 Mohr units of volume at 17.5°. Using a 200 mm. tube,

$$c = 0.32856\,Pol$$

Exactly the same value is reached from the basis of the observation[2] that one Ventzke degree for milk-sugar is equal to 0.3452 circular degrees, with sodium light. As $c = 0.9518\,\alpha$, we have also

$$c = 0.9518 \times 0.3452\,Pol,$$

or

$$c = 0.32856\,Pol.$$

179. **The Determination of Sugar in Milk** is carried out, according to Schmoeger,[3] in this way:

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[1] This is the specific rotation of milk-sugar at 17.5°.

[2] Landolt "Ueber polarimetrisch-chemische Analyse," Ber d chem Ges, **21**, 191 (1888)

[3] Ber d milchwirthschaftl Instituts zu Proskau, 1883-4

1. According to Hoppe-Seyler, 50 cc. of milk is boiled wit 25 cc. of a 20 to 25 per cent. lead acetate solution, to the sti warm liquid, 5 cc. of a 10 per cent. alum solution is added, an then the mixture is cooled, filled up to 100 cc. and filtered The volume of the precipitate is in the mean 3 cc., and is t be taken into consideration.

2. 100 cc. of milk is coagulated by addition of 6 cc of 10 to 1 per cent. acetic acid and after standing half an hour is filtered A slight turbidity from fat globules does no harm. 50 cc. o the filtrate is heated to boiling with 3 to 4 cc. of basic leac acetate solution (sp. gr. 1.2), and, after cooling, water is addec to make up for loss on evaporation The liquid is then filtered.

3 100 cc. of milk is coagulated as before or by addition of 6 cc. of 10 to 15 per cent. sulphuric acid, but instead of separating the proteids by basic lead acetate, 50 cc. of the filtrate is treated in the cold with 5 cc. of commercial phosphotungstic acid, then filtered and polarized. The result must be multiplied by 1.1.

As in methods 2 and 3, the volume of the precipitate is taken as 6 cc., in the mean; it is advisable to add just 6 cc of acid for coagulation, because then the concentration of the milk-sugar in the filtrate (whey) will be exactly the same as in the original milk. Besides, in methods 2 and 3, the disadvantageous dilution of the liquid containing the milk-sugar to the double volume is avoided

A comparison of the three processes led to the conclusion that method 3 gives about 0.15 per cent. higher values than method 2, and that this in turn gives again 0.15 per cent higher results than method 1. Schmoeger traces these differences to this, that in mixing the milk with the lead solution, milk-sugar, or possibly some other right-rotating substance not clearly known, is thrown out of solution. This is certainly the case when, after using an excess of lead solution, the filtrate is alkaline. Schmoeger is, therefore, of the opinion that the third method gives correct results, possibly a few hundredths too high.

But, on the other hand, the results obtained by method 1 agree very closely with the gravimetric analyses according to Tollens, and those by method 2 with the gravimetric analyses according to Soxhlet with fair accuracy. It is not possible, therefore, to give a final decision as to which is the more accurate procedure. An advantage in the polarimetric method over the gravimetric is found in the greater rapidity and convenience with which it may be carried out.

III. Determination of Glucose (Dextrose, Grape-Sugar) (Crystallized $C_6H_{12}O_6 + H_2O$)

180. Tollens[1] has given this formula showing the dependence of the specific rotation of dextrose anhydride on the percentage strength of the solution.

$$[\alpha]_D^{20} = 52.50 + 0.0188\,p + 0.000517\,p^2.$$

From this we have for:

$p =$	5	10	15	20	25	30
$[\alpha] =$	52.61	52.74	52.90	53.08	53.29	53.53
$p =$	35	40	45	50	55	60
$[\alpha] =$	53.79	54.08	54.39	54.73	55.10	55.49

The specific rotation increases then appreciably with the concentration. But for solutions up to 15 per cent. strength, without very great error, $[\alpha]$ can be taken as equal to 52.80. If we substitute this value in the equation $[\alpha] = \frac{100\,\alpha}{l\,p\,d}$, this formula follows for calculating the percentage strength from the observed angle α,

$$p = 1.894\,\frac{\alpha}{l\,d},$$

and using a 2 dm. tube,

$$(1) \qquad p = 0.947\,\frac{\alpha}{d}.$$

If not the percentage strength but the concentration of the solution is to be found, that is, the number of grams of sugar in 100 cc. of solution, then this formula may be transformed into the simpler one,

$$(2) \qquad c = 0.947\,\alpha.$$

The error made by neglecting the variation of the specific rotation with the strength of solution reaches then in the most unfavorable case 0.03 per cent., assuming that the observed angle of rotation α is measured at 20° with use of sodium light.

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[1] Tollens: Ber. d. chem. Ges., 17, 2238 (1884).

For greater concentrations (15 to 50 per cent.) Landolt[1] has calculated the following formula, for finding the percentage strength, from the observations of Tollens:

$$(3)\qquad p = 0.948\,\alpha - 0.0032\,\alpha^2,$$

where α is the rotation for a 2 dm. tube.

Dextrose may be determined by use of the Ventzke saccharimeter also, since, according to the observations of Hoppe-Seyler,[2] its rotation dispersion is very nearly the same as that of quartz It has been found by direct experiments[3] that for dextrose, 1° V. $= 0.3448 \pm 0.0008$ circular degrees (Na light). If we represent by *Pol.* the number of Ventzke degrees read off for a 2 dm. tube at 20°, the formulas just developed may be transformed into these ·

$$\text{(I)}\qquad p = 0.3265\,\frac{Pol}{d} \qquad [p = 0 \text{ to } 15]$$

$$\text{(II)}\qquad c = 0.3265\,Pol \qquad [c = 0 \text{ to } 16]$$

$$\text{III)}\qquad p = 0.3269\,Pol - 0.000381\,Pol^2 \qquad [p = 0 \text{ to } 50]$$

Thus, for example, a grape-sugar solution which shows a rotation of 34.48° in an instrument with circular degrees must polarize exactly 100 in the Ventzke saccharimeter. We have by Formula (3),

$$p = 0.948 \times 34.48 - 0.0032 \times 34.48^2 = 28.88 \text{ per cent.},$$

and likewise by Formula (III),

$$p = 0.3269 \times 100 - 0.000381 \times 100^2 = 28.88 \text{ per cent.}$$

But, nevertheless, one cannot expect as accurate results from the saccharimeter as from the instrument with circular degrees, because the value of a circular degree in saccharimeter degrees might not be the same for all instruments and all solutions.

For this reason, and because the specific rotation of dextrose is dependent on the temperature and concentration, a normal weight cannot be definitely fixed, which may be dissolved to make 100 Mohr cc. and give directly, in the saccharimeter, the percentage strength of dextrose in the dissolved substance. But, however, for most practical needs, sufficiently accurate values may be derived from the following considerations

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[1] Landolt. Ber. d. chem Ges, **21**, 199 (1888)

[2] See Landolt *Ibid.*, **21**, 194 (1888)

[3] Ztschr anal Chem, **5**, 412 (1866)

For dilute solutions we have above,

$$c = 0.3265 \times Pol,$$

$$Pol = \frac{c}{0.3265}.$$

cordingly, a liquid which contains 32.65 grams of dextrose 100 cc. must be able to polarize 100° V But as the Mohr it of volume is related to the cubic centimeter as 00234 1, then to secure the same concentration in a Mohr 0 cc. flask there must be weighed out, in vacuo, 32.65 × 00234 = 32.73 grams of the substance containing dextrose 32 71 grams in air with brass weights

Also, we obtain the normal weight of dextrose, *N*, when multiply the normal weight of saccharose, 26.048, by the lation of their specific rotations We obtain in this way ·

For 5 per cent solutions . $N = 26.048 \times \frac{66.47}{52.61} = 32.91$ grams.

For 15 per cent solutions . $N = 26.048 \times \frac{66.52}{52.90} = 32.75$ grams

For 25 per cent solutions $N = 26.048 \times \frac{66.49}{53.29} = 32.50$ grams

The normal weight varies, therefore, for solutions practically ie most used, containing 0 to 25 per cent of dextrose, between 32.9 and 32.5 grams. In weighing out a dextrose substance then, one must take into consideration whether it contains much or little of the sugar The normal weight derived bove for dilute solutions, 32.71 grams, would hold, according to the last calculation, for solutions containing from 17 to 8 per cent. of dextrose

If the amount of dextrose hydrate, instead of that of the nhydride, is desired the result must be multiplied by the reation of the two molecular weights $\frac{198}{180} = 1.1$.

Finally, it must be remembered that solid dextrose dissolved in water exhibits birotation, which is destroyed by allowing he solution to stand twenty-four hours, or by warming.

181. **The Determination of Dextrose in Diabetic Urine** may be advantageously made when the amount present is more than about 0.2 gram in 100 cc. With smaller amounts, or where the greatest accuracy is desired, as in normal urines or in phys-

iological investigations, the chemical methods of determination yield more reliable results. It must first be seen whether or not the color of the urine will permit a direct polarization, using if necessary, a tube only 100 mm. long, or after diluting to the double volume. If the urine is not perfectly clear it should be filtered as quickly as possible through soft filter-paper. If the urine is too dark, 100 cc. should be precipitated by 10 cc. of basic lead acetate solution, and the filtrate tested, or it may be shaken in a flask with some blood-charcoal and then filtered. In the first case, the result of the polarization must be multiplied by 1.1 on account of the dilution. But in both cases, a part of the grape-sugar may be removed from the urine, at least this has been shown after application of basic lead acetate, and it may be assumed for the charcoal from the experience gathered in the clarification of dark sugar sirups. These errors may be eliminated by making a parallel experiment with like quantities of clarification agents and normal urines whose sugar content is brought to that of the urine under investigation, and which is polarized before and after application of the clearing agent.

If the diabetic urine contains albuminous substances they may, on account of their left rotation, make the sugar content appear much too low, and it is, therefore, necessary to remove them 100 cc of urine is heated in a dish to boiling and then enough dilute acetic acid is added to give an acid reaction and throw down the albumin as a flocculent precipitate Then the liquid is filtered, the filter washed, and the filtrate made up to 100 cc Or a measured volume of urine is acidified with acetic acid and then enough concentrated sodium sulphate solution added to bring the volume to double the original. If the liquid is now heated, the albumin separates completely and may be filtered off.

Bile acids, which have a right-hand rotation, are not present in urine in amount sufficient to cause an error in the above process.

The fact that the albumin in urine rotates the plane of polarization to the left very nearly as much as grape-sugar does to the right, furnishes us with a very convenient means of determining the amount of albumin in urine polarimetrically If polarization of the urine be observed at the same tempera- e (17.5°) before and after precipitation of the albumin, and he same degree of concentration, we obtain from the dif- ence, *D*, of the two readings, with a 2 dm. tube, the ount of albumin, Al, in the liquid, from the formula de- ed above for the determination of the grape-sugar content dilute solutions.

$$\text{Al} = 0.947\,D.$$

The firm of Schmidt and Haensch makes a half-shadow in- ument with circular degrees on the Laurent system (§111 to 13) for urine analysis A sodium flame serves for illumina- n In order to avoid the necessity of calculating the sugar or umin content from the rotation read off in circular degrees, cording to the above equation, tubes of 188.6 and 94.3 mm. in ngth (better 189.4 and 94.7) are furnished with the instru- ent, the shorter one for dark liquids, which lengths are so osen that 1° or 2° of polarization corresponds exactly to 1 ram of grape-sugar in 100 cc. of the liquid analyzed

The same firm makes also half-shadow instruments with edge-compensation for urine analysis, permitting the use of hite light (§133–§134), the scale of which is so arranged that y employing a 2 dm. tube, the amount of grape-sugar in 100 c. may be read off directly The vernier reads to $^1/_{10}$ per cent

IV. Determination of Maltose

(Crystallized $C_{12}H_{22}O_{11} + H_2O$. Right-rotating)

182. Meissl[1] gives the following formula for the dependence f the specific rotation on the percentage strength and the tem- erature *t*.

$$[\alpha]^t_D = 140.37 - 0.0184\,p - 0.095\,t,$$

which holds good for $p = 5$ to 35 and $t = 15°$ to $35°$. We have from this, when $t = 20°$, for

$p =$	5	10	15	20	25	30	35
$[\alpha]^{20}_D =$	138.38	138.29	138.20	138.11	138.02	137.92	137.82

Parcus and Tollens[2] found a somewhat lower value for the specific rotation from a concentration of 10 grams in 100 cc. at 20°,

$$[\alpha]^{20}_D = 136.85 \text{ to } 136.96,$$

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[1] J prakt Chem, [2] **25**, 114 (1882)

[2] Parcus and Tollen: Ann Chem (Liebig), **257**, 160 (1890)

while for this concentration the specific rotation according to Meissl is 138.3.

For the practical determination of maltose by the optical method a mean value of

$$[\alpha]_D^{20} = 137.5$$

may be considered as sufficiently exact. Then at 20°,

$$137.5 = \frac{100\,\alpha}{l \times c},$$

$$c = 0.7273\,\frac{\alpha}{l},$$

and by the use of a 2 dm. tube at 20°,

$$c = 0.3636\,\alpha.$$

Meissl gives this formula for the temperature of 17.5° .

$$c = 0.362\,\alpha$$

As freshly prepared solutions show a rotation which is too low, they must be warmed before polarization or allowed to stand some hours.

V. Determination of Galactose

($C_6H_{12}O_6$. Right-rotating.)

183. According to Meissl[1] the change in the specific rotation with the percentage strength and the temperature is given by the formula,

$$[\alpha]_D^t = 83.88 + 0.0785\,p - 0.209\,t,$$

in which $p = 5$ to 35 per cent., $t = 10$ to 30°.

According to Rindell,[2]

$$[\alpha]_D^t = 83.04 + 0.199\,p - (0.276 - 0.0025\,p)t,$$

for $p = 12$ to 20 per cent., $t = 4°$ to 40°.

If we take $t = 20°$, we have then for

$p =$	5	10	15	20	25	30	35
$[\alpha]_D^{20}$ Meissl	80.10	80.49	80.88	81.27	81.66	82.06	82.45
$[\alpha]_D^{20}$ Rindell		80.01	81.25	82.50			
$[\alpha]_D^{20}$ Kent and Tollens[3]		80.7 81.4	81.7				
$[\alpha]_D^{20}$ Parcus and Tollens[4]		80.33					

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[1] J. prakt. Chem., [2], **22**, 97 (1880).

[2] Rindell Ztschr. Rübenzucker-Ind., **30**, 163 (1880).

[3] *Ibid.*, **35**, 36 (1885).

[4] Parcus and Tollens Ann. Chem. (Liebig), **257**, 160 (1890).

For solutions with 0 to 15 per cent., and possibly even to 20 er cent., we may take, therefore, the Meissl value of 80.88 or $p = 15$ as the mean specific rotation of galactose at 20°. From this there follows:

$$c = 1.236 \frac{\alpha}{l},$$

nd for a 2 dm. tube at 20°,

$$c = 0.618\,\alpha.$$

Freshly dissolved galactose also exhibits birotation, which t the ordinary temperature reverts to the normal rotation after lapse of six hours.

VI. Determination of Camphor, $C_{10}H_{16}O$

184. The easy determination of camphor in the optical way has become of greater importance since the introduction of rticles made of celluloid, a mixture of nitrocellulose and camphor. According to Foerster[1] the determination of camphor n celluloid is made best as follows:

About 10 grams of celluloid, containing 2 to 3 grams of amphor, is saponified with four times its weight of 10 per cent. sodium hydroxide solution until all has dissolved, and he mixture is then diluted to 250 cc. Of this, 120 to 150 cc. s distilled off, the camphor, in vapor, passing over completely with the steam. To the distillate, collected in a graduated eceiver, 25 to 30 cc. of benzene is added and the mixture well shaken; the volume of the benzene, which dissolves the camphor, is read off and a part is then taken for polarization at 20°.

The author carried out special tests to determine the rotation of camphor in benzene, and as a standard he used pure camphor with melting-point at 178.7°, which had been recrystallized several times from 50 per cent. alcohol. Solutions up to the concentration of 40 grams of camphor in 100 cc. ($d\,^{20}/_4$) were tested at 20° and with sodium light. The specific rotation as dependent on the concentration may be expressed by this formula:

$$\text{(I)} \qquad [\alpha]_D^{20} = 39.755 + 0.1725\,c.$$

From this the concentration c may be calculated as a function of the angle of rotation α:

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[1] Ber. d. chem Ges, 23, 2981 (1890)

$$\text{(II)} \qquad c = 115\ 205\left[-1+\sqrt{1+0.04367\frac{\alpha}{l}}\,\right]$$

From the observations themselves, the following direct relation between concentration and rotation may be derived:

$$\text{(III)} \qquad c = 2.4683\frac{\alpha}{l} - 0.01747\left(\frac{\alpha}{l}\right)^2$$

This formula was calculated from the earlier determinations of Landolt,[1] showing the specific rotation of camphor in benzene,

$$[\alpha]_D^{20} = 39.19 + 0.17084\,c,$$

and from experiments by Rimbach,[2] the following for concentrations between 10 grams and 53 grams:

$$[\alpha]_D^{20} = 40.21 + 0.1309\,c + 0.000269\,c^2.$$

These two formulas agree closely with that of Foerster. Test experiments showed that from 99 to 99.3 per cent. of the camphor taken could be found, which, considering the method of separation used, is a satisfactory result

In fats and oils also, camphor may be determined by the optical process. According to Foerster it is best, in such cases, to first distil the camphor from the substance under investigation by aid of a current of steam. When about 250 cc of distillate has been collected in the receiver, this is then used as the distillation flask and the rest of the operation is carried out as with celluloid.

If, in place of benzene, alcohol is chosen as the solvent for the camphor, the concentration of the solution may be found by the following formulas, according to Landolt:[3]

$$c = 2.3614\frac{\alpha}{l} - 0.01158\left(\frac{\alpha}{l}\right)^2$$

or

$$c = -177\ 53 + \sqrt{31516.45 + 845.74\frac{\alpha}{l}}$$

These obtain for concentrations between 0 and 50 grams in 100 cc , and for a temperature of 20°.

VII. Determination of Cinchona Alkaloids

185. The specific rotation of the cinchona alkaloids and their

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[1] Landolt · Ann. Chem (Liebig), **189**, 334 (1877)

[2] Rimbach Ztschr phys Chem , **9**, 698 (1892)

[3] Landolt Ber. d chem. Ges., **21**, 204 (1888).

NGALO

st important salts has frequently been the subject of ex-
ded investigations ; numerous observations have been made
ecially by Hesse,[1] Oudemans,[2] and Lenz,[3] by which the con-
nts of rotation for quinine, hydroquinine, cinchonine, quini-
e, and cinchonidine have been determined with such accu-
y that they may be used in testing other preparations as to
ir purity, or in finding the composition of mixtures

Vith all these alkaloids, the specific rotation varies in
rked degree with the nature of the solvent, and moreover
s smaller, the greater the concentration and the higher the
nperature. Hesse measured the rotation of solutions which
itained from 1 to 10 grams of substance in 100 cc., accord-
to the degree of solubility As solvents, alcohol of 97
ume per cent. was used for the pure alkaloids, and either
re water or dilute hydrochloric or sulphuric acid of known
ength for the salts. Lenz employed as a solvent a mixture
2 volumes of chloroform and 1 volume of 97 per cent.
ohol, and determined the specific rotation in solutions of 1
3 per cent strength

Notwithstanding these fundamental investigations, no
thod is yet known by which the alkaloids in extracts of
ichona bark or in the quinine of commerce may be found by
e optical process. This is due partly to the fact, already re-
red to, that the specific rotation is in a large measure de-
ndent on the external conditions under which the solutions
question must be tested, and partly to this, that the optical
alysis of a mixture of several active substances cannot, in
neral, be made with accuracy, and even when only two or
ree are in solution, while in any case the qualitative compo-
ion of the mixture must be known, which can be determined
ly by the methods of chemical analysis Finally, this diffi-
lty is met with in the optical determination of the alkaloids
the extracts from cinchona bark, that these extracts contain
yellow coloring-matter which cannot be separated alone, and
e presence of which makes the observation in the polarimeter
icertain.

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[1] Hesse Ann Chem (Liebig), **176**, 203, **182**, 128

[2] Oudemans *Ibid.*, **182**, 33

[3] Lenz Ztschr anal Chem., **27**, 549 (1888)

In such investigations, therefore, it is customary to e the extraction and separation of the alkaloids by cher methods, and then to resort to the optical observations to trol the results of the chemical analysis or to test the separ alkaloids as to their purity.

For the determination of the quantitative composition mixture of alkaloids, the specific rotation may be employe all those cases where the analysis of a mixture of two kn alkaloids only is involved The following conditions t obtain:

Of the mixture of two alkaloids, c grams is weighed dissolved to make 100 cc., and then the angle of rotation is found in a tube of l dm. length, from which may be culated the specific rotation of the mixture, $\alpha = \frac{100\,\alpha}{l \times c}$. If mixture contains x per cent. of one alkaloid, whose spe rotation is $[\alpha]_x$, and $y = 100 - x$ per cent. of the other c stituent with the specific rotation $[\alpha]_y$, then

$$x \times [\alpha]_x + (100 - x)\,[\alpha]_y = 100\,[\alpha]$$

and consequently,

$$x = 100\,\frac{[\alpha] - [\alpha]_y}{[\alpha]_x - [\alpha]_y}$$

$$y = 100\,\frac{[\alpha]_x - [\alpha]}{[\alpha]_x - [\alpha]_y}.$$

In this way, it is possible to analyze mixtures of any act substances, provided the specific rotations of the pure su stances are known and are not subject to too great variatic within the limits of the concentrations employed.[1] But, in a event, it is advisable to take the concentration of the mixtu only as great as appears necessary for the accurate calculat of the specific rotation.

Hesse[2] has already employed this general method to dete mine the amount of cinchonidine sulphate in the commerc quinine sulphate, nearly free from other alkaloids.

He proceeded in this way, by taking first, of the sulphate question, an amount corresponding to 2 grams of the anhydro salt, dissolving in a 25 cc. flask in 10 cc. of normal hydr loric acid, and filling to the mark with water at 15° C. fter complete solution and mixing, the liquid was filtered to a 220 mm. jacketed tube and polarized at 15° in a Wild olaristrobometer. If α represents the angle of rotation of the nhydrous quinine sulphate under these conditions ($\alpha = -$ 0.309° was found), and β the rotation of the anhydrous cinhonidine sulphate ($\beta = -26.598°$ was observed), and γ, nally, the angle of rotation of the mixture taken for the nalysis, then the amount of cinchonidine sulphate, y, in the nit of weight of the mixture is given by

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[1] See Hesse. Ann Chem (Liebig), **182**, 146 and 152, Oudemans · *Ibid*, **182**, 63,

[2] Hesse *Ibid*, **205**, 217 (1880)

$$y = \frac{\alpha - \gamma}{\alpha - \beta} = \frac{-40.309 - \gamma}{-13.711},$$

hile the amount of the quinine sulphate is

$$x = \frac{\gamma - \alpha}{\alpha - \beta} = \frac{\gamma + 26.598}{-13.711}.$$

VIII. Determination of Cocaine

186. The specific rotation of cocaine, $C_{17}H_{21}NO_4$, in chloroorm, and of the hydrochloride, $C_{17}H_{21}NO_4.HCl$, in a mixture f 60 parts of absolute alcohol and 90 parts of water, has been etermined by O Antrick.[1] He found for a preparation of the ase of the greatest possible purity:

$$[\alpha]^{20}_D = -15.827 - 0.00585\, q,$$

r,

$$[\alpha]^{20}_D = -16.412 + 0.00585\, p.$$

This gives then for

$p =$	5	10	15	20	25	30
$[\alpha]^{20}_D =$	− 16.38	− 16.35	− 16.32	− 16.29	− 16.26	− 16.24

For solutions containing up to 30 per cent. of cocaine, the value, $[\alpha]^{20}_D = -16.32$, may be taken as the basis of the calculation of the percentage strength. We have

$$-16.32 = \frac{100\,\alpha}{l p d},$$

$$p = -6.13\,\frac{\alpha}{l d},$$

and with use of a 2 dm. tube:

$$p = -3.06\,\frac{\alpha}{d},$$

$$c = -3.06\,\alpha.$$

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[1] O. Antrick Ber d. chem Ges., **20**, 310 (1887)

The specific rotation of the hydrochloride of cocaine h been even more fully investigated by Antrick. The followi formula expresses the results obtained from observations (four preparations which in their properties differed but litt from each other :

$$[\alpha]_D^{20} = -67.982 + 0.1583c;$$

this holds for $c = 0$ to 25, and for true cubic centimeters $(d_4^{20}$

It follows then for $[\alpha]_D^{20}$ with

$c =$	5	10	15	20	25
$[\alpha]_D^{20} =$	-67.19	-66.40	-65.61	-64.82	-64.02

The change in the specific rotation with the concentratio is here so considerable that it is not possible to make a mea value of this rotation the basis of a calculation of the concentration from the observed angle of rotation In the formul

$$c = \frac{100\,\alpha}{[\alpha] \times l},$$

we have to take for $[\alpha]$ that value from the above series which comes the nearest to the expected concentration, or we may make use of the following equation, derived directly from the formula for the specific rotation

$$(1) \qquad c = 214.72 - \sqrt{46106.8 + 315.86\,\alpha}$$

which holds for the 2 dm. tube, $t = 20°$, and $c = 0$ to 25°

Finally, the angles of rotation, $\alpha = -13.280°$ and $\alpha = -25.927$, given by Antrick for the concentration $c = 10$ and $c = 20$, may be employed to express c as directly related to the observed angle α The formula for this reads

$$(2) \qquad c = -0.7337\,\alpha + 0.001454\,\alpha^2,$$

which holds for the 2 dm tube within the given limits.

In using either of these formulas, care must be taken to see that α is introduced with the proper sign, that is the negative sign. In using polarization tubes of other length than 2 dm. the value of the angle read off must be corrected before it is substituted in either of the two formulas, which are based on observations with 2 dm. tubes.

The agreement in the results which may be obtained by the two formulas is shown in the following table :

a.	c Concentration calculated by Formula (1).	c Concentration calculated by Formula (2)	Difference $c_1 - c_2$
5	3.710	3.705	+0.005
10	7.485	7.482	+0.003
15	11.331	11.332	−0.001
20	15.252	15.256	−0.004
25	19.250	19.251	−0.001
30	23.333	23.320	+0.013

IX. Determination of Nicotine, $C_{10}H_{14}N_2$

187.—A new method for the quantitative determination of icotine by the polariscope has been devised by M Popoici.[1] The extraction of the nicotine from tobacco is best accomplished by Kissling's process · 20 to 40 grams of homoeneous dry tobacco powder is moistened with 10 cc. of a ilute alcoholic sodium hydroxide solution (6 grams of NaOH issolved in 100 cc. of 57 per cent. alcohol) and extracted hree to four hours with ether in the Soxhlet apparatus. The ther extract is treated with 10 cc. of a rather strong solution f phosphomolybdic acid in nitric acid and shaken, by which neans the nicotine is thrown down with other bases (mainly mmonia) in the form of a quickly subsiding precipitate. Then he supernatant ether is poured off and enough water is added o the residue to make a total volume of 50 cc, and finally 8 rams of finely powdered barium hydroxide is added. In this way the nicotine is obtained as a free base in alkaline solution, which, after some hours with frequent shaking, is poured off from the yellow precipitate, and polarized The following table was obtained from experiments with known amounts of nicotine

Grams of nicotine in 50 cc of solution	Rotation in 2 dm tube Minutes	1 Minute of rotation corresponds to nicotine in grams
2.00	337	0.00594
1.75	298	0.00588
1.50	258	0.00582
1.25	217	0.00576
1.00	175	0.00572
0.75	133	0.00564
0.50	89	0.00562
0.25	45	0.00556

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[1] Popovici · Ztschr physiol. Chem., 13, 445 (1889)

If an alcoholic solution of nicotine, containing no other active substances, is to be examined the following formula by Landolt[1] may be employed to find the nicotine content:

$$(1) \qquad p = 311.58 - \sqrt{97082.5 - 449.64\frac{\alpha}{ld}},$$

which holds for a temperature of 20°, the density d_4^{20}, and between 10 and 90 per cent. of nicotine.

Further, with reference to the nicotine concentration:

$$(2) \qquad c = 0.704\frac{\alpha}{l} - 0.000525\left(\frac{\alpha}{l}\right)^2,$$

which obtains for 20° and $c = 10$ to 90.

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[1] Landolt Ber d. chem. Ges, **21**, 203 (1888).

PART SIXTH

Constants of Rotation of Active Bodies

In the following tabulation the data on the specific rotation f all active bodies in any degree important have been included nd the literature has been fully considered to the middle of 896. Only a few of the still later observations could be given place.[1] Only such specific rotations have received consideration for which the data necessary for calculation (density, concentration, temperature) were given in the original papers.

In explanation of the signs employed, see Part First, §§ 1 and 2 of this book.

I. Hydrocarbons

(See also Terpenes and Camphor.)

Ethylamyl b. p. 91°, $d^{20} = 0.6895$, $[\alpha]_D = +3.93°$ [2]
$t = 17°$, $[\alpha]_D = +6.23°$ } [3]
$= 60°$, $= +6.09°$ }
Propylamyl: $t = 16°$, $[\alpha]_D = +6.44°$ } [4]
$= 54°$, $= +6.25°$ }
Isobutylamyl $t = 20°$, $[\alpha]_D = +5.88°$ } [5]
$= 52°$, $= +5.66°$ }
$= 21°$, $= +5.31°$ } [6]
$= 65°$, $= +5.20°$ }
Diamyl b. p. 159°–162°, $d^{22} = 0.7463$, $[\alpha]_D = +8.69°$ [7]
$t = 21°$, $[\alpha]_D = +12.08°$ } [8]
$= 78°$, $= +12.06°$ }
$= 19°$, $= +10.01°$ [9]

These bodies were all made from active amyl iodide.

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[1] [In the translation the most important observations to the middle of 1900 have been included.—Tr.]

[2] Just. Ann. Chem. (Liebig), **220**, 154.

[3] Welt. Compt. rend., **119**, 743.

[4] Welt: *Loc. cit.*

[5] Welt: *Loc. cit.*

[6] Guye and Amaral: Arch. sc. phys. Genève, [3], **33**, 409.

[7] Just: *Loc. cit.*

[8] Welt: *Loc. cit.*

[9] Guye and Amaral: *Loc. cit.*

2. Alcohols with One Atom of Oxygen

1. *l*-Amyl Alcohol $C_2H_5.CH_3.CH.CH_2OH$. Commerci fermentation alcohol: $\alpha_D = -2°$ to $-4°$ for 1 dm.

Preparations purified from inactive isomers by Le Bel method (repeated treatment with gaseous hydrochloric aci through which the inactive part is first converted into am chloride and may be separated by distillation) gave ·

$\alpha_D = -4\ 53°$ to 4.63° for 1 dm. $[\alpha]_D = -5.7°$ whe $d = 0\ 81$.[1] $[\alpha]_D = -5.2$, $d^{22} = 0\ 818$, boiling-point 128.5° t 129° (768 mm).[2]

According to Schutz and Marckwald,[3] these preparation were not yet pure.

Derivatives of *l*-Amyl Alcohol

Amyl chloride b. p 97 to 99°, $d^{15} = 0.886$, $[\alpha]_D = +1.24$ [4]
Amyl bromide: " 117 " 120°, " $= 1\ 225$, " $= +3\ 5$
Amyl iodide " 144 " 145°, " $= 1.54$, " $= +5\ 41$
Amyl iodide " 144 " 146°, $d^{20} = 1\ 538$, " $= +4\ 55$[5]

Acid Esters and other Amyl Compounds

For these bodies, which are all liquid, the following dat have been given, and by:

1 Walden.[6] Rotation of the amyl alcohol used, $[\alpha]_D = -4.78$

	Boiling-point	mm	d	$[\alpha]^{20}_D$.
Amyl acetate..............	141–142°	.	0 8734	+ 2 50
Amyl *n*-butyrate...........	176	752	0.8685	+ 2 97
Amyl *iso*-butyrate..........	167–168	752	0 8662	+ 2 83
Amyl chloracetate...... ...	190–191	..	1.0438	+ 3 16
Amyl brom-*n*-butyrate.. ...	140	55	1.1899	+ 2 27
Amyl brom-*iso*-butyrate....	129	50	1.1851	+ 2 53
Diamyl oxalate............	260–261	757	0.9626	+ 4.93
Diamyl fumarate...........	172–173	21	0 9760	+ 5.69
Diamyl maleate..	167–168	21	0.9829	+ 4.35
Diamyl chlorfumarate......	188	23	1 0593	+ 5.74
Diamyl chlormaleate	176	23	1.0568	+ 4 60
Diamyl *o*-phthalate	232	43	1.0315	+ 3.88
Amyl acetic acid	212–213	..	0 9146	+ 8 53

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[1] Le Bel Bull. soc chim, [2], **21**, 542, Compt rend, **77**, 1021.
[2] Rogers J Chem Soc, **63**, 1131
[3] Schütz and Marckwald Ber d. chem Ges, **29**, 59.
[4] Le Bel Bull soc chim, [2], **25**, 545
[5] Walden Ztschr. phys Chem, **15**, 647.
[6] *Ibid*, **15**, 642 ff

	Boiling-point.	mm	d	$[\alpha]_D^{20}$
Ethyl amylacetate	180–182	760	0.8765	+ 6.56
Amyl amylacetate	228–230	775	0.8631	+ 7.01
Diamyl acetate	262–263	760	0.8894	+ 18.27
Ethyl diamylacetate	235–238	760	0.8701	+ 17.99
Amyl diamylacetate	268–270	775	0.8594	+ 13.96
Amyl malonic acid	(m.p. 90°–91°, acetone $c = 6.67$)			+ 5.25
Diethyl amylmalonate	244–246	..	0.9665	+ 10.14
Diethyl diamylmalonate	280	760	0.9445	+ 5.82
Ethyl amylacetoacetate	228–232	..	0.9455	+ 11.48
Ethyl diamylacetoacetate	265	768	0.9120	inactive
Diethyl amyl-*p*-nitrobenzyl malonate	(m.p. 51°, acetone $c = 20$)			+ 1.25
Amyl piperidine	185–186	..	0.8459	+ 7.94

2 WALDEN[1] Rotation of the amyl alcohol used, $[\alpha]_D = -4.7°$

	Boiling-point	mm	d	$[\alpha]_D^{20}$.
Amyl *i*-lactate	105°	22	0.9672	+ 2.64
Amyl *l*-lactate	101–102	17	0.9667	− 3.93
Amyl *i*-mandelate	170–171	20	1.0520	+ 2.76
Amyl *l*-mandelate	166–167	17	1.0530	− 94.02
Amyl *i*-phenylchloracetate	166–167	20	1.0832	+ 3.23
Amyl *d*-phenylchloracetate	169–170	24	1.0826	+ 26.79
Diamyl *i*-malate	191–192	20	1.0180	+ 3.50
Diamyl *l*-malate	191–192	20	1.0176	− 6.88
Diamyl *i*-chlorsuccinate	187–188	22	1.0314	+ 3.75
Diamyl *d*-chlorsuccinate	187	22	1.0305	+ 25.15
Diamyl racemate	208	20	1.064	+ 3.37
Diamyl *d*-tartrate	208	20	1.0636	+ 17.73

3 WALDEN.[2] Rotation of the amyl alcohol used, $[\alpha]_D = -4.8°$

	Boiling-point	mm	d	$[\alpha]_D^{20}$
Diamyl maleate	170°	29	0.9747	+ 4.62
Diamyl chlormaleate	185	25	1.0555	+ 4.03
Diamyl brommaleate	175–177	13	1.1561	+ 4.58
Diamyl bromfumarate	185–187	15	1.1683	+ 5.99
Diamyl citraconate	179	25	0.9661	+ 4.14
Diamyl itaconate	170–172	10	0.9657	+ 4.97
Diamyl antidimethylsuccinate	168–169	15	0.9469	+ 3.42
Diamyl paradimethylsuccinate	185	30	0.9452	+ 3.66
Diamyl mesotartrate	203–204	17	1.0658	+ 4.77
Diamyl racemate	201–202	16	1.064	+ 3.37

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[1] Ztschr. phys. Chem., 17, 705 ff

[2] *Ibid*, 20, 378

4 WALDEN[1] Rotation of the amyl alcohol not given

	Boiling-point	mm	d.	$[\alpha]_D^{20}$.
Amyl *n*-butyrate	178–179°	765	0.8690	+ 2.81
Amyl crotonate	190–192	750	0.8958	+ 4.24
Amyl isobutyrate	170–171	765	0.8619	+ 3.10
Amyl methacrylate	75	20	0.8781	+ 3.51
Diamyl succinate	178–180	25	0.9592	+ 3.76
Diamyl fumarate	165	10	0.9696	+ 5.93
Diamyl chlorsuccinate	187–188	22	1.0314	+ 3.75
Diamyl chlorfumarate	187	14	1.0560	+ 5.78
Diamyl methylsuccinate	172	18	0.9529	+ 3.67
Diamyl mesaconate	183–184	20	0.9698	+ 5.93
Triamyl tricarballylate	240	25	0.9973	+ 4.01
Triamyl aconitate	241–243	26	1.0029	+ 6.16
Amyl hydrocinnamate	172	28	0.9721	+ 2.26
Amyl cinnamate	192	29	0.9992	+ 7.51
Amyl phenylpropiolate	210	55	1.0035	+ 5.58
Amyl α-naphthoate	222	25	1.0605	+ 5.28
Amyl β-naphthoate	265	100	1.0531	+ 9.34

5 GUYE AND CHAVANNE[2] Rotation of the common amyl alcohol used, $[\alpha]_D = -4.4$. Rotation of the *sec*-amyl alcohol not given

	$[\alpha]_D^{20-22}$	$[\alpha]_D^{60-70}$
Amyl formate	+ 2.01	+ 1.98
Amyl acetate	+ 2.53	+ 2.51
Amyl propionate	+ 2.77	+ 2.68
Amyl butyrate	+ 2.69	+ 2.54
Amyl palmitate	+ 1.45	+ 1.16
	d	$[\alpha]_D$
sec-Amyl acetate	0.962	— 4.06
sec-Amyl propionate	0.895	— 8.55
sec-Amyl butyrate	0.889	— 8.25
prim-Amyl benzoate	0.988	+ 4.96
prim-Amyl phenylacetate	0.982	+ 3.84
prim-Amyl phenylpropionate	0.976	+ 2.15

6. GOLDSCHMIDT AND FREUND.[3] Rotation of the amyl alcohol used, $[\alpha]_D = -4.29$. The following solid esters were used in chloroform solution

	p	$[\alpha]_D$
Amyl phenylcarbaminate	5.248	+ 4.19
Amyl *o*-tolylcarbaminate	5.328	+ 2.66
Amyl *m*-tolylcarbaminate	5.306	+ 3.85
Amyl *p*-tolylcarbaminate	5.277	+ 4.47

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[1] Ztschr. phys. Chem., 20, 573 [2] Compt rend, 120, 452 [3] Ztschr phys. Chem., 14, 394.

7. GUYE AND GOUDET.[1]

	$[\alpha]_D$
r-Amyl *d*-amylacetate	+ 4.36
l-Amyl *r*-amylacetate	+ 1.54
r-Amyl *d*-amylmalonate	+ 6.10
l Amyl *r*-amylmalonate	+ 3.48

GUYE AND AMARAL[2] investigated the following derivatives of *l*-amyl alcohol at different temperatures

	t	$[\alpha]_D$	*t*	$[\alpha]_D$
Amyl alcohol	16°	— 4.52	76°	— 4.12
Valeraldehyde	15	+ 14.09	72	+ 11.14
Valeraldoxime	20	+ 11.13	51	+ 9.97
Amyl bromide	18	+ 2.51	62	+ 2.07
Amyl iodide	18	+ 3.67	60	+ 3.13
Amyl acetate	18	+ 2.54	57	+ 2.51
Amyl chloracetate	27	+ 3.00	51	+ 2.97
Amyl amine	18	— 0.87	62	— 0.99
Diamyl amine	18	+ 5.59	57	+ 4.71

Amylamine hydrochloride[3] Water, $p = 7.84$, $[\alpha]_D = +12.7°$

Mixed Amyl Ethers

GUYE AND CHAVANNE[4] give the following data.

	Boiling-point	*d*	$[\alpha]_D$
Methyl-amyl ether	87.5– 88.5°	0.754	+ 0.39°
Ethyl-amyl ether	107.5–109	0.759	+ 0.61
Propyl-amyl ether	125 –127	0.783	+ 0.90
Isobutyl-amyl ether	145 –147	0.773	+ 0.96
Isoamyl-amyl ether	145 –147	0.774	+ 0.70
Cetyl-amyl ether	145 –147	0.805	+ 0.31
Benzyl-amyl ether	231 –232	0.911	+ 1.83

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[1] Compt rend., **121**, 827.

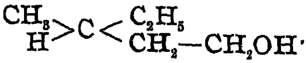
[2] Arch. Sc. phys. Genève [3], **33**, 409; Compt. rend., **120**, 1345.

[3] Plimpton J Chem. Soc., **39**, 332; Compt rend., **92**, 531, 883

[4] Compt rend., **120**, 452

WELT[1] gives for other ethers .

	t	$[\alpha]_D$
Phenol-amyl ether	17°	+ 4.0°
p-Cresol-amyl ether	19	+ 4.26
o-Cresol-amyl ether	20	+ 3.86
m-Cresol-amyl ether	22	+ 3.93
4,5-Methyl-propyl-phenol-amyl ether	18	+ 4.17
4,6-Methyl-propyl-phenol-amyl ether	19	+ 4.01



2 *d*-HEXYL ALCOHOL, $\substack{CH_3\\H}>C<\substack{C_2H_5\\CH_2-CH_2OH}$. From Roman camomile oil.

Boiling-point 154° (at 758 mm.),

$$d_{15} = 0.829,\ t = 17°,\ [\alpha]_D = +8.2°.$$[2]

3. METHYL-HEXYL CARBINOL,

$$\substack{CH_3\\C_2H_5}>CH.CH_2\ CH_2.CHOH.CH_3$$

Obtained by reduction of the following compound

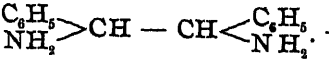
$$t = 24°,\ [\alpha]_D = +4.69°.$$[3]

Methyl-hexyl ketone. By saponification of amyl acetoacetate.

$$\left.\begin{array}{l} t = 21°,\ [\alpha]_D = +5.06° \\ t = 57°,\ [\alpha]_D = +4.41° \end{array}\right\}$$[4]

3. Alcohols with Two to Four Atoms of Oxygen

A few optically active compounds of this kind are known, such as *l*-propyleneglycol, but the optical constants of none of them have been accurately determined. As derivatives of such alcohols we may consider:



Diphenyl-ethylene-diamine, $\substack{C_6H_5\\NH_2}>CH - CH<\substack{C_6H_5\\NH_2}$. — Obtained by reduction of benzyl dioxime. Melting-point 90° to 92°. Split as bitartrate.

$$\left.\begin{array}{ll} \text{Ether.} & t = 15° \\ d\text{-Base.} & [\alpha]_D = +134.8° \\ l\text{-Base.} & [\alpha]_D = -128 \end{array}\right\}$$[5]

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[1] Ann chim phys, [7], 6, 115

[2] van Romburgh Rec trav chim, 5, 220

[3] Welt Compt rend, 119, 855

[4] Welt *Loc cit*

[5] Feist and Arnstein, Ber d. chem Ges, 28, 3167

1, 5-Tetrahydronaphthylene-diamine. Split as bitartrate. he hydrochlorides in aqueous solution gave at 17 5° :

$$\left.\begin{array}{l} d\text{-Base. } c = 2.44,\ [\alpha]_D = +\ 8.15^\circ \\ l\text{-Base. } c = 3.96,\ [\alpha]_D = -\ 7.5 \end{array}\right\}^{1}$$

4. Alcohols with Five Atoms of Oxygen

Pentitols, $CH_2OH.(CH.OH)_3.CH_2OH$.

ARABITOL, melting-point 102°. Held by Kiliani,[2] but im-operly, as inactive

Cold saturated borax solution. $p = 9.05$, $[\alpha]^{20}_D = -\ 5.3^\circ$. fter 36 hours still unchanged.[3]

XYLITOL, inactive Bertrand's statement, $[\alpha] = +\ 0.5^\circ$ is rong.[4]

ADONITOL, inactive, also in borax solution [5]

RHAMNITOL, $CH_3.(CH.OH)_4\ CH_2OH$ Triclinic prisms. Melting-point 121°. Water, $p = 8.648$, $[\alpha]^{20}_D = +\ 10.7^\circ$.[6]

5. Alcohols with Six Atoms of Oxygen

Hexitols, $CH_2OH.(CH\ OH)_4.CH_2OH$.

d-MANNITOL The behavior in aqueous solution, the action f borax and other salts, also of acid sodium and ammonium molybdates, are given in § 70, pp. 253 to 256

In alkaline solution, left rotating. Water with 8 per cent of NaOH, $p = 8$, $[\alpha]_D = -\ 3\ 4^\circ$.[7]

Derivatives :

Nitromannitol, $C_6H_8(O.NO_2)_6$

Ether . ...$p = 4.2$, $[\alpha]_j = +\ 70\ 2^\circ$ [8]
Alcohol ....$p = 2$, $[\alpha]_j = +\ 63\ 7$ [9]
Alcohol ....$c = 7\ 5$, $[\alpha]_D = +\ 40$ [10]

Hexachlorhydrin, $C_6H_8Cl_6$:

Benzene........ .. ..$[\alpha]_D = +\ 18\ 5^\circ$ [11]

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[1] Bamberger Ber d chem Ges , **23**, 292

[2] *Ibid.*, **20**, 1234

[3] Fischer, Piloty *Ibid.*, **24**, 521

[4] Bull soc chim , [3], **5**, 554.

[5] Fischer· Ber d chem. Ges., **26**, 633

[6] Fischer, Piloty *Ibid* , **23**, 3102

[7] Müntz, Aubin · Ann chim. phys , [5], **10**, 566.

[8] Krecke Arch Néerl., VII, 1872

[9] Krecke. *Ibid* , VII, 1872.

[10] Krusemann Ber d. chem Ges., **9**, 1468.

[11] Mourges Compt. rend., **111**, 112

l-MANNITOL. In borax solution strongly left rotating.[1]

Isomannitol. Water, $p = 6$, $[\alpha]_D = + 91.36°$. Alcohol $p = 3$, $[\alpha]_D = + 94.66°$.[2]

DULCITOL. Inactive, also in borax solution.[3] Bouchardat's statement[4] that diacetyl and tetraacetyl dulcitol are slightly right rotating has been contradicted by Crossley.[5]

SORBITOL See statement in § 70.

d-TALITOL The aqueous solution is slightly right rotating, the borax and alkali solutions slightly left rotating.[6]

RHAMNOHEXITOL, $CH_3.(CH.OH)_5.CH_2OH$. Water, $c = 10.4$, $t = 20$, $[\alpha]_D = + 14.0°$.[7]

d-INOSITOL, $C_6H_{12}O_6$ and hydrate, $C_6H_{12}O_6 + 2H_2O$ Water, $p = 10$ (anhyd), $[\alpha]_D = + 65.0°$.[8]

Methyl-d-inositol, pinitol, $C_6H_{11}O_6.CH_3$.

Alcohol .... $[\alpha]_D = + 65.51°$ [9]
Water .. .. $[\alpha]_D = + 65.7$ [10]

Matezitol, identical with *pinitol.* Melting-point, 187°.

Water .... $[\alpha]_D = + 66.0°$ [11]
Water, $c = 3.625$, $[\alpha]_D = + 64.7$ [12]
Water, $c = 11.867$, $[\alpha]_D = + 65.2$ [13]

l-INOSITOL. Water, $[\alpha]_D = - 65°$.[14]

Methyl-l-inositol, quebrachitol. Water, $[\alpha]_D = - 80°$.[15]

6. Alcohols with Seven and More Atoms of Oxygen

Heptitols, $CH_2OH.(CH.OH)_5.CH_2OH$.

d-MANNOHEPTITOL, $C_7H_{16}O_7$, perseitol. Perseitol from *Laurus*

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[1] Fischer Ber d chem Ges., **23**, 375
[2] Fauconnier Bull soc. chim., [2] **41**, 119
[3] Fischer, Hertz Ber d chem Ges., **25**, 1247
[4] Ann chim phys, [4], **27**, 68, 145
[5] Ber d. chem Ges, **25**, 2564
[6] Fischer· *Ibid*, **27**, 1524
[7] Fischer, Piloty *Ibid*, **23**, 3827
[8] Maquenne. Compt rend, **109**, 968
[9] Maquenne. *Ibid*, **109**, 812
[10] Combes *Ibid*, **110**, 46.
[11] Combes: *Ibid*, **110**, 46.
[12] Girard *Ibid*, **110**, 84.
[13] Girard *Ibid*, **110**, 84
[14] Tanret. *Ibid*, **109**, 908
[15] Tanret *Loc. cit*

ea L., is inactive according to Muntz and Marcano,[1] but ording to Gernez,[2] slightly left rotating, and in aqueous so-on for $c = 7.36$, $[\alpha]^{15}_{D} = - 1\ 22°$.

ariety from *d*-mannoheptose: for cold saturated borax so-on, $c = 8$, right rotating, $[\alpha]^{20}_{D} = + 4\ 75°$.[3]

)n the action of acid sodium and ammonium molybdate, see , p. 256.

OLEMITOL, $C_7H_{16}O_7$ Water, $p = 10$, $[\alpha]^{20}_{D} = + 1.92°$.[4]

ALAHEPTITOL, $C_7H_{16}H_7$. Water + borax, $p = 8.8$, $[\alpha]^{2}_{D}$ $- 4\ 35°$.[5]

-GLUCOOCTITOL, $C_8H_{18}O_8$. Water, $p = 10\ 24$, $d = 1.038$, $]^{20}_{D} = + 2°$.[6] After addition of borax three times as strong.

7 Acids with Two Atoms of Oxygen

l-VALERIC ACID, methyl-ethyl acetic acid, $C_2H_5\ CH_3\ CH.$ $)_2H$ From *l*-amyl alcohol.

[From amyl alcohol of $[\alpha]_{D} = - 4\ 4°$ Boiling-point, 173° 174°, (730 mm.)] $d^{22} = 0\ 938$, $[\alpha]_{D} = + 13.64°$ [7]

[From amyl alcohol of $[\alpha]^{22}_{D} = - 5.2°$. Boiling-point, 4 5° (768 mm.).] $d^{22}_{22} = 0\ 936$, $[\alpha]^{22}_{D} = + 13.9°$,[8] $[\alpha]^{11}_{D} = 11\ 27°$, $[\alpha]^{59}_{D} = + 10\ 84°$ [9]

According to Schutz and Marckwald,[10] valeric acids with the tations given must contain still about 20 to 25 per cent of purities For the pure substance $[\alpha]_{D}$ must be + 17° to °, see *l*-valeric acid

Derivatives

VALERALDEHYDE, Boiling-point, 92.5°, $d^{0} = 0\ 8209$, $[\alpha]_{D}$ $+ 1\ 7°$[11] (maximum value) $[\alpha]^{15}_{D} = + 14\ 09°$, $[\alpha]^{72}_{D} = 11\ 14°$.[12]

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[1] Ann chim phys, [6], **3**, 279

[2] Compt rend, **114**, 480

[3] Fischer and Passmore Ber d chem Ges., **23**, 2226

[4] Fischer *Ibid.*, **28**, 1973

[5] Fischer Ann. Chem (Liebig), **288**, 147

[6] Fischer *Ibid.*, **270**, 99

[7] Guye and Chavanne Compt rend, **116**, 1455

[8] Roger, J Chem Soc, **63**, 1134

[9] Guye and Amaral, Arch. sc phys Genève, [3], **33**, 409

[10] Ber d chem Ges, **29**, 59

[11] Erlenmeyer and Hell, Ann Chem. (Liebig), **160**, 257

[12] Guye and Amaral Arch sc phys. Genève, [3], **33**, 409

VALERALDOXIME, $[\alpha]^{20}_{D} = + 11.13°$; $[\alpha]^{51}_{D} = + 9\ 97°$ [1]

ESTERS OF *d*-VALERIC ACID.

	B p (730 mm)	d^{22}	$[\alpha]_D$	
Methyl ester	113 to 115°	0.882	+ 16 83°	From valeri acid.[2] $[\alpha] =$ + 13 64
Ethyl ester	131 to 133	0.864	+ 13 44	
N-Propyl ester.......	154 to 157	0.860	+ 11 68	
N-Butyl ester	173 to 176	0.856	+ 10.60	
Isobutyl ester	165 to 167	0 855	+ 10 48	
Benzyl ester	246 to 250	0 982	+ 5 53	

For further observations of Guye and Guerchgorine, se Compt. rend., 124, 230

l-VALERIC ACID. First obtained by Schutz and Marckwald by resolution of the synthetic acid (from ethyl-methyl-maloni acid), by aid of brucine Boiling-point, 173° to 174° Th rotation for the following colors was determined by use of th ray filter method, §158.

	Wave-lengths λ	Temp 20° $d^{20}_{4} = 0\ 934$	Temp 30° $d^{30}_{4} = 0\ 926$
Red	665.9 μμ	[α] = — 13 50°	[α] = — 12 91°
Yellow (Na).........	589.2	17 85	17 02
Green	533 0	22 57	21.44
Light blue...	488 5	27.75	26 29
Dark blue............	448.2	34 19	32.63

d-CAPROIC ACID, *β*-*β*-methyl-ethyl-propionic acid, C_2H_5 CH_3 $CH.CH_2CO_2H$

From *d*-hexyl alcohol. Boiling-point, 196° to 198° (770 mm.), $d^{15} = 0.930$. $[\alpha]^{19}_{D} = + 8.92°$.[4]

HEXYL ESTER OF CAPROIC ACID Boiling-point, 233° to 234° (768 mm.), $d^{15} = 0.867$ $[\alpha]^{19}_{D} = + 12.86°$.[5]

For other esters see Guye and Guerchgorine.[6]

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[1] Guye and Amaral *Loc cit*

[2] Guye and Chavanne Compt rend , 116, 1455

[3] Ber d chem Ges., 29, 52

[4] v Romburgh Rec trav chim Pays-Bas , 5, 222

[5] v Romburgh

[6] Compt rend , 124, 230

l-AMYLACETIC ACID, $C_2H_5.CH_3$ $CH.(CH_2.CH_2CO_2H)$. By ponification of amyl acetoacetate.

ıd........ $t = 20°$, $[\alpha]_D = + 8\ 44°$, $t = 54°$ $[\alpha]_D = + 7.64°$[1]
thyl ester.... $t = 25$, " $= + 6.71$, $t = 75$, " $= + 5\ 92$
hyl ester .... $t = 21$, " $= + 6\ 66$, $t = 72$, " $= + 5\ 87$

For amyl esters see under amyl alcohol.

PARASORBIC ACID, sorbinoil, $C_6H_8O_2$. $[\alpha]_j = + 40.8°$.[2]

d-PIPECOLINIC ACID, $C_5H_{10}NCO_2H$ Obtained by resolution the racemic acid by means of *d*-tartaric acid.

Water, $p = 19\ 93$, $[\alpha]_D^{25} = + 33\ 4°$
Water, $p = 9\ 92$ " $= + 35\ 7$

l-PIPECOLINIC ACID. Made by aid of *l*-tartaric acid.

Water, $p = 9\ 92$, $[\alpha]_D^{25} = - 34\ 8°$[3]

8. Acids with Three Atoms of Oxygen and Derivatives

d-LACTIC ACID, CH_3 $CH\ OH.CO_2H$ *Sarcolactic acid* (paractic acid). As first shown by Wislicenus,[4] certain amounts f the ester anhydride, $C_6H_{10}O_5$, and of the lactide, $C_6H_8O_4$, are lways formed in concentrating aqueous solutions of sarcolactic cid; both of these bodies have a strong left rotation The ight rotation of the acid is, therefore, found too small. On tanding, the anhydrides in aqueous solution pass gradually nto acids and the rotation increases. See §75, p 280 As ighest values there were found.

ı $42\ 97$, $[\alpha]_D = + 2\ 91°$ [5]
$32\ 84$, $3\ 46$
$21\ 25$, $2\ 66$
$7\ 38$, $2\ 78$

Also by Hoppe-Seyler and Araki [6]

$p = 39\ 85$, $d = 1\ 0907$, $[\alpha]_D^{11\ 5}$ $+ 3\ 48$ to $3.54°$
$22\ 90$, 1.0538, 2.53
$11\ 19$, $1\ 0273$, $1\ 57$ to $1\ 89$

For the rotation of the pure acid made by Krafft and Dyes,[7] no data have been given.

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[1] Welt. Compt rend., **119**, 855
[2] Doebner Ber. d chem Ges., **27**, 348
[3] Mende *Ibid*, **29**, 2887
[4] Ann Chem (Liebig), **167**, 302.
[5] Wislicenus *Ibid.*, **167**, 324 to 327.
[6] Ztschr. physiol. Chem., **20**, 369
[7] Ber. d. chem Ges., **28**, 2589.

Anhydride.—A preparation which contained 84 per cent. of $C_6H_{10}O_5$ and 16 per cent. of $C_3H_4O_2$ gave, in alcoholic solution, $c = 19.54$, $[\alpha]_D = -85.9°$.[1]

If but a few per cent. of the anhydrides are present in lactic acid solutions, they exhibit left rotation.

d-Lactic Acid Salts.

These all show left rotation.

Zinc Salt, $Zn(C_3H_5O_3)_2 + 2H_2O$ The rotation of aqueous solutions increases slightly on dilution. There was found for the hydrated salt

1. $c = 16.05$,[2]	$[\alpha]_D = -6.36°$	2. $p = 9.08$,	$[\alpha]_D = -6.56°$[3]
11.01,[2]	6.36	8.29,	6.64
7.47,	6.83	6.53,	6.84
6.13,	7.41	5.89,	6.83
5.26,	7.60	4.18,	7.55

3. $c = 7.49$, $[\alpha]_D = -6.83°$[4]

Zinc Ammonium Salt, $Zn\,NH_4(C_3H_5O_3)_3 + 2H_2O$

Water, $c = 8.00$, $[\alpha]_D = -6.06°$.[4]

Calcium Salt, $2Ca(C_3H_5O_3)_2 + 9H_2O$

Water, $c = 7.23$, $[\alpha]_D = -3.87°$[5]
Water, $p = 6.25$, $[\alpha]_D = -3.85$[6]

Lithium Salt, $Li.C_3H_5O_3$.

Water, $p = 5$ to 12, $[\alpha]_D = -10.95$ to $12.28°$[6]

d-Lactic Acid Esters.

Methyl ester. .... $d_4^{13} = 1.100$, $[\alpha]_D = -11.1°$ [7]
Propyl ester..... $d_4^{19} = 1.004$, $[\alpha]_D = -17.06$

For further determinations see Frankland and Henderson[8]

l-LACTIC ACID. By resolution of fermentation lactic acid by means of strychnine (§33), or by the action of *Bacillus acidi laevo-lactici* on cane-sugar

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[1] Wislicenus Ann Chem (Liebig), 167, 321

[2] Supersaturated Wislicenus *Ibid*, 167, 332

[3] Hoppe-Seyler and Araki. Ztschr physiol Chem, 20, 371

[4] Purdie J. Chem Soc, 63, 1154

[5] Wislicenus. *Loc. cit*

[6] Hoppe-Seyler and Araki. *Loc cit*

[7] Walker J Chem Soc, 67, 916

[8] Proc Chem. Soc, 11, 54 (1895).

Water, $c = 64.8$, $[\alpha]_D = -4.3°$[1]
Water, $p = 12.43$, $d = 1.0348$, $t = 23.3$, $[\alpha]_D = -4.72°$[2]
Water, $p = 6.57$, $d = 1.0192$, $t = 23.6$, " $= -5.86$

l-Lactic Acid Salts

They all show right rotation in aqueous solution.

Zinc Salt, $Zn(C_3H_5O_3)_2 + 2H_2O$.

1. $c =$ 16.08 12.66 5.85 5.57 [3]
   $[\alpha]_D = +5.4$ $+5.2$ $+6.5$ $+6.3°$
2. $c = 7.484$, $[\alpha]_D = +6.81°$.[4]
3. $p = 6.751$, $d_4^{17} = 1.0318$, $[\alpha]_D = +6.32°$.[5]

Zinc Ammonium Salt, $Zn.NH_4(C_3H_5O_3)_3 + 2H_2O$.

$p = 8.63$, $d_4^{18} = 1.035$, $[\alpha]_D^{18} = +6.49°$ [6]
$p = 5.87$, " $= 1.024$, " $= +7.07$

Lithium Salt, $LiC_3H_5O_3$

$p = 3.7$ to 9.1, $[\alpha]_D = +13.5$ to $12.7°$[7]

Sodium Salt See § 57, p. 202.

Ethyl Ester

$d_4^{19} = 1.030$, $[\alpha]_D = +14.52°$[8]
$[\alpha]_D = +14.19°$[9]
$[\alpha]_D = +8.6$[10]

Chlor-propionic Acid, $CH_3.CHCl.CO_2H$.

Methyl ester of the *d*-acid. $d_4^{20} = 1.1520$, $[\alpha]_D = +19.01°$ [11]
Ethyl ester of the *d*-acid... " $= 1.0888$, " $= +12.86$
Methyl ester of the *l*-acid.. $d_4^{5} = 1.158$, " $= -26.83$ [12]
Ethyl ester of the *d*-acid.. $d_4^{11.5} = 1.087$, " $= +19.51$
Propyl ester of the *d*-acid.. $d_4^{6} = 1.065$, " $= +11.0$

Brom-propionic Acid, $CH_3.CHBr.CO_2H$.

Methyl ester of the *d*-acid $d_4^{17} = 1.482$, $[\alpha]_D = +42.65°$ [13]
Ethyl ester of the *l*-acid. . $d_4^{10} = 1.386$, " $= -31.45$
Propyl ester of the *d*-acid.. $d_4^{14} = 1.315$, " $= -21.98$

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[1] Schardinger · Wien Monatsh , **11**, 551
[2] Hoppe Seyler and Araki Ztschr physiol Chem , **20**, 369
[3] Schardinger *Loc cit.*
[4] Purdie J Chem. Soc , **63**, 1154
[5] Purdie and Walker *Ibid.*, **61**, 762
[6] Purdie and Walker *Ibid* , **61**, 761
[7] Hoppe-Seyler and Araki · Ztschr physiol. Chem , **20**, 372
[8] Walker J. Chem. Soc , **67**, 917
[9] Klimenko J russ. chem. Ges , **12**, 30.
[10] Frankland and Henderson . Proc Chem. Soc., **11**, 54 (1895)
[11] Walden Ber d chem. Ges , **28**, 1293
[12] Walker J Chem Soc., **67**, 918.
[13] Walker . *Loc cit.*

ALKYL OXYPROPIONIC ACIDS. Purdie and Lander[1] hav pared a number of active compounds by resolution of ma methoxypropionic, ethoxypropionic, and propoxyprop acids by aid of cinchonidine and morphine. The author lieve that a nearly complete separation of one compone each case was secured and numerical values are given fo free acids and their sodium and calcium salts as follows:

l-Methoxypropionic acid,	water....	$c = 13.475$	$[\alpha]_D =$	$- 71.0$
Sodium salt,	water....	$c = 16.530$	"	$- 49.4$
Calcium salt,	water....	$c = 9.53$	"	$- 38.0$
d-Ethoxypropionic acid,	water....	$c = 29.374$	"	$+ 56.9$
Sodium salt,	water..	$c = 17.965$	"	$+ 48.0$
Calcium salt,	water....	$c = 26.875$	"	$+ 38.4$
d-Propoxypropionic acid,	water....	$c = 11.450$	"	$+ 55.63$
Sodium salt,	water....	$c = 30.750$	"	$+ 48.94$
Calcium salt,	water....	$c = 12.010$	"	$+ 48.54$

Purdie and Irvine[2] have determined the optical behavio methoxypropionic and ethoxypropionic acids and esters pared from active lactic acid.

β-OXYBUTYRIC ACID, $CH_3.CH.OH.CH_2.CO_2H$

The *l*-form has been found in diabetic urine.[3]

Acid. Water, $[\alpha]_D = - 20.6°$ [4]

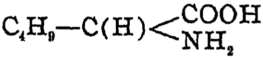
$[\alpha]_D = - 23.4$.[5]

Sodium Salt. Water, $p = 32.1$, $[\alpha]_D = - 15°$.[4] $p = 2$ $d^{20}_4 = 1.0900$, $[\alpha]_D = - 13.93°$.[6]

Silver Salt. $[\alpha]_D = - 10.1°$;[4] $c = 1.4$, $[\alpha]_D = - 8.64°$

A series of esters of *d*- and *l*-oxybutyric acid has been vestigated by Guye and Jordan.[8]

d-**LEUCIN**,



$C_4H_9{-}C(H){<}\begin{matrix}COOH\\NH_2\end{matrix}$

In hydrochloric acid solution, left rotating.

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[1] J Chem Soc., **73**, 862 (1898)

[2] *Ibid*, **75**, 483 (1899)

[3] Minkowski Ber. d. chem Ges., **17**, Ref 334, 535. Kulz Ber. d. chem Ges., Ref 534; **18**, Ref 451.

[4] Minkowski

[5] Külz: Ber. d. chem. Ges., **20**, Ref. 591

[6] Deichmüller, Szymanski and Tollens: Ann Chem. (Liebig), **228**, 94.

[7] Kulz.

[8] Compt rend, **120**, 1274 and **120**, 630.

From conglutin:

20 per cent HCl .... $c = 4.73$, $[\alpha]_D = -17.5^\circ$

From active (conglutin) leucin:

20 per cent HCl.......... ... $c = 5.00$, $[\alpha]_D = -17.3^\circ$

From inactive leucin ·

20 per cent. HCl....... .. . $c = 4.37$, $[\alpha]_D = -17.4^\circ$[1]

By resolution of the α-amido acid from fermentation caproic acid by means of *Penicillium glaucum*, Schulze obtained an active leucin, different from the ordinary leucin, and which was left rotating in hydrochloric acid:[2]

Acid ... . $c = 4$ to 5, $[\alpha]_D = -26.0^\circ$ to -26.5°

l-LEUCIN. In aqueous solution, left rotating,[3] in acid or alkaline solution, right rotating.

From casein.

10 per cent HCl .... $c = 6.4$ $[\alpha]_D = +17.54^\circ$ [4]
Alkaline .... $c = 5.6$ " $= +6.65$

From beet molasses

4 per cent NaOH· .... $c = 2.371$, $t = 20^\circ$, $[\alpha]_D = +8.05^\circ$[5]

From conglutin:

19 per cent HCl............ $c = 5.00$, $[\alpha]_D = +17.31^\circ$[6]
20 per cent HCl· .... $c = 4.73$, " $= +17.3$[7]

RICINELAIDIC ACID, $CH_3(CH_2)_7CHOH\ CH\ CH\ (CH_2)_8$-COOH. Melting-point, 53°.

Acetone .... $c = 5$ to 15, $[\alpha]_D = +4.8$ to 5.4° [8]
Alcohol ... . $c = 12$, " $= +6.67^\circ$

RICINOLEIC ACID. Isomeric with ricinelaidic acid

Acetone...... . ... $c = 4.8$ to 21, $t = 22^\circ$, $[\alpha]_D = +6.27$ to 7.5°[9]

RICINSTEAROLEIC ACID, $C_{17}H_{30}OH\ COOH$ Melting-point, 51°.

Acetone...... $c = 6.4$, $[\alpha]_D = +13.67^\circ$[9]

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[1] Schulze and Bosshard. Ztschr physiol. Chem, **10**, 143, Schulze and Likiernik Ber d chem Ges, **24**, 472

[2] Ber d chem Ges, **26**, 56.

[3] Lewkowitsch · *Ibid.*, **17**, 1439

[4] Mauthner · Ztschr physiol. Chem., **7**, 222

[5] Landolt · Ber d. chem Ges, **27**, 2838

[6] Schulze and Bosshard, Ztschr. physiol. Chem., **9**, 100

[7] Schulze · Ber. d chem. Ges, **26**, 56.

[8] Walden *Ibid.*, **27**, 3471.

[9] Walden

d-MANDELIC ACID, $C_6H_5.CHOH.CO_2H$. Melting-po 132.8°.

By resolution of the inactive acid by means of the cinc nine salt or by *Penicillium glaucum.*[1]

Water . . . . $p = 2$ 886, $d = 1.0055$, $[\alpha]_D^{20} = 156$

Cinchonine Salt.

Chloroform + alcohol . . . . . $p = 1.944$, $[\alpha]_D^{20} = +153.91°$

On the resolution of mandelic acid see papers by Rimbac and by McKenzie[3]

l-MANDELIC ACID. Melting-point, 132.8° From amygda or by resolution of the inactive acid (through the cinchoni salt or by *Saccharomyces ellipsoideus* and a schizomycite)[4]

The specific rotation of solutions in water and glacial acet acid decreases on dilution according to the following formulas

Water . . . . $q = 91$ to 97, $[\alpha]_D^{20} = -212$ 52 + 0.5777

Glacial acetic acid . . . . $q = 82$ to 97, " $= -209.95 + 0$ 2714

An increase in temperature of 10° decreases the specific rot tion of the solution by about 5°.

On the behavior of methoxy-, ethoxy-, and propoxy-subst tuted *l*-mandelic acid, see McKenzie.[6]

l-Cinchonine salt, more soluble than the *d*-salt.

Alcohol + chloroform . . . . $p = 1.946$, $[\alpha]_D^{20} = +91.64°$[7]

Walden[8] gives the following constants for *l*-mandelic acid and its derivatives.

Free acid	Acetone	$c = 2.50$,	$[\alpha]_D^{22} = -148.0°$
(m p 131°–132°)	Water	2.45,	− 153 06
Amide	Acetone	2.50,	− 66.6
(m p. 122°–122 5°)	Acetone	1.50,	− 66 7
Methyl ester	Carbon disulphide . .	3.33,	− 214.1
(b. p 160°, 32 mm.)	" " . .	1 67,	− 217.0
	Acetone	3.33,	− 110.2

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[1] Lewkowitsch, Ber d. chem Ges, **16**, 1568

[2] *Ibid*, **32**, 2385

[3] J Chem Soc, **75**, 964

[4] Lewkowitsch Ber. d chem Ges., **16**, 1571

[5] Lewkowitsch *Ibid*, **16**, 1567

[6] J Chem Soc, **75**, 753 (1899)

[7] Lewkowitsch Ber d. chem. Ges., **16**, 1574

[8] Ztschr phys. Chem, **17**, 706 ff.

Ethyl ester	Superfused	$d = 1.1270$,		— 123.12
(b.p. 150°, 21 mm)	Chloroform	$c = 6.67$,	$[\alpha]_D =$	— 128 4
(m. p. 35°)	"	3.33,		— 126.4
	Acetone	5.81,		— 90 62
	"	1.16,		— 87.1
	Carbon disulphide	5.00,		— 180.0
	" "	2.50,		— 180 0
	" "	0.88,		— 180.5
Isobutyl ester	Superfused	$d = 1\ 0870$,		— 100 73
(b. p. 159°, 19 mm. solid)	Carbon disulphide	$c = 5\ 0$,		— 146 6
	" "	2.5,		— 144.0
i-Amyl ester	b.p 166°–167°, 17 mm	$d = 1.0531$,	$[\alpha]_D =$	— 96 46
l-Amyl ester	" 166°–167°, 17 "	1 0530,	"	— 94 02
Acetylmandelic acid, methyl ester	" 177°, 45 "	1.1546,	"	— 146.37
Propionylmandelic acid, methyl ester	" 184°, 45 "	1.1261,	"	— 135.5
Propionylmandelic acid, ethyl ester,	Superfused	$d = 1.0936$,	"	— 113.7
(b p 177°, 30 mm	Chloroform	$c = 10\ 0$	"	— 110 8
m p. 33°)	"	5 0	"	— 109 4
	Carbon disulphide	5 0	"	— 131 5
	" "	2 5	"	— 126 8
Valerylmandelic acid, ethyl ester,	b p 173°–174°, 18 mm	$d = 1\ 0544$,	"	— 97 06
	Carbon disulphide	$c = 10\ 0$,		— 117 25
	" "	5 0,		— 116 9
Acetylmandelic acid, m.p. 56°	Acetone	3 33,		— 156 4

In addition Walden[1] gives the following observations

d-PHENYLCHLORACETIC ACID, C_6H_5 CHCl.COOH. From *l*-mandelic acid. Melting-point, 56° to 58°.

Benzene	$c = 3\ 33$,	$[\alpha]_D =$	+ 132.13°
"	5.33,		+ 131.6
Carbon disulphide	4.00,		+ 131.3
Chloroform	5.33,		+ 107.9

Chloride, liquid. b p. 120° (23 mm.)	Carbon disulphide	$c = 6\ 0$,	$[\alpha]_D =$	+ 158 33°
Methyl ester, liquid b. p. 135°–136° (22 mm.)		$d = 1\ 2087$		+ 107.55
Ethyl ester, liquid b p. 162° (45 mm.)		$d_4^{20} = 1.1594$,		+ 25 19
	In carbon disulphide, $p = 4.96$,	$d = 1.2527$,		+ 26 39
n-Propyl ester, b. p. 180°, 60 mm.		1.1278,		+ 23 94

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[1] Ztschr. phys Chem, 17, 714; Ber d chem Ges, 28, 1295.

i-Amyl ester,	"	167°–168°,	20 mm.	$d = 1.0828$,	$[\alpha]_D = + 23$ 3
l-Amyl ester,	"	169°–170°,	24 "	1 0826,	+ 26.7

d-PHENYLBROMACETIC ACID, $C_6H_5.CHBr$ CO_2H. Fro *l*-mandelic acid. Melting-point, 76° to 78°.

Benzene .. .. $c = 8.0$, $[\alpha]_D = + 45.4°$.

Bromide,	liquid.	b p. 145°–147°,	24 mm	$d^{20}_4 = 1$ 853,	$[\alpha]_D = + 44.5$
Methyl ester,	"	" 172°,	53 "	1 4421,	+ 29.8
Ethyl ester,	"	" 164°,	20 "	1.3893,	+ 16 5
Isobutyl ester,	"	" 167°-168°,	19 "	1.2892,	+ 9.77

d-ISOPROPYLPHENYLCHLORACETIC ACID, $C_3H_7.C_6H_4.CHC$ CO_2H Melting-point, 75° to 76°.

Benzene .... $c = 3.0$, $[\alpha]_D = + 23.3°$.

d-ISOPROPYLPHENYLGLYCOLLIC ACID, $C_3H_7.C_6H_4.CHOH$ CO_2H [1]

By crystallization of the cinchonine salt of the inactive acid Melting-point, 153° to 154°.

Alcohol .... $c = 4$ 0568, $t = 17°$, $[\alpha]_D = + 134.9°$

Quinine salt m p. 192°–193°.[2]

Alcohol . ..... $c = 0.9248$, $t = 24°$, — 79 4°

Cinchonine salt. m p 201° [2]

Alcohol .... . $c = 2.3014$, $t = 13°$, + 136 8°

l-ISOPROPYLPHENYLGLYCOLLIC ACID. By crystallization o the quinine salt of the inactive acid.[2] Melting-point, 153° tc 154°.

Alcohol.. .... $c = 4.0916$, $t = 17°$, $[\alpha]_D = - 135°$

Quinine salt m p 204°–205° [2]

Alcohol.......... $c = 0$ 3800, $t = 13°$, — 118.4°

Cinchonine salt. m p. 167° [2]

Alcohol. .... $c = 1$ 3308, $t = 24°$, + 83.4°

d-TROPIC ACID, $C_6H_5.CH(CH_2OH).CO_2H$ Melting-point, 127° to 128°, $[\alpha]_D = + 71.4$. Solvent and concentration not given.[3]

l-TROPIC ACID. Melting-point, 123°, $[\alpha]_D = - 65.2°$.[3]

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[1] Fileti J prakt. Chem , [2], 46, 561 ; Gazz. chim ital , 22, 2, 395

[2] Fileti . *Loc cit*

[3] Ladenburg and Hundt. Ber d chem. Ges , 22, 2591.

9. Acids with Four Atoms of Oxygen and Derivatives

d-GLYCERIC ACID, $CH_2OH.CH.OH.CO_2H$.

The racemic acid obtained by oxidation of glycerol with nitric acid has been resolved by means of *Penicillium glaucum*[1] and *Bacillus ethaceticus*.[2] In the first case, the left-rotating acid remains unattacked, and the right-rotating in the second case.

Here, as with the lactic acids, the rotation determinations are inaccurate, because on evaporation of the aqueous solutions a change into a left-rotating anhydride seems to take place ·

$c = 20$, acid (calcium salt and oxalic acid), $[\alpha]_D^{12} = +2.14°$ [3]

Salts of the d-Acid. Left rotating

Detailed observations have been made by Frankland and Appleyard,[4] who give the following figures :

Formula	c	$t°$	$[\alpha]_D$	
			hydrated salt	anhydrous salt
$Li(C_3H_5O_4)$	10	11		$-20.66°$
$Na(C_3H_5O_4) + \frac{1}{2}H_2O$	10	12		-16.13
$K(C_3H_5O_4)$	11.635	18		-16.46
$K(C_3H_5O_4)(C_3H_6O_4)$	10.359	18	..	-9.24
$NH_4(C_3H_5O_4)$	10.610	20		-18.05
$Ca(C_3H_5O_4)_2 + 2H_2O$	10	17	-11.66	-13.34
$Sr(C_3H_5O_4)_2 + 3H_2O$	10	15	-10.08	-11.91
$Ba(C_3H_5O_4)_2 + 2H_2O$	10		-9.07	-10.01
$Mg(C_3H_5O_4)_2 + H_2O$	10	19	-18.65	-20.08
$Zn(C_3H_5O_4)_2 + H_2O$	10	16	-22.18	-23.63
$Cd(C_3H_5O_4)_2 + 1\frac{1}{2}H_2O$	10	19	-14.11	-15.29

Esters of the d-Acid. Left rotating.

Frankland and MacGregor[5] have investigated the following liquid esters ·

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[1] Lewkowitsch : Ber d. chem. Ges., **16**, 2720

[2] Frankland and Frew J Chem. Soc., **59**, 96.

[3] Frankland and Frew : *Ibid.*, **59**, 101.

[4] J. Chem. Soc., **63**, 296.

[5] *Ibid.*, **63**, 511, 1410.

Methyl ester	d^{15}_{15} = 1.2798,	$t = 15°$,	$[\alpha]_D$ = −
Ethyl ester	1.1921,	15°,	−
N-Propyl ester	1.1448,	17°,	−
Isopropyl ester	1.1303,	15°,	−
N-Butyl ester	1.1084,	17°,	−
Isobutyl ester	1.1051,	18°–19.5°,	−
Sec-Butyl ester	1.1052,	19°,	−
Heptyl ester	1.0390,	18°,	−
Octyl ester	1.0263,	19°,	−

On amyl esters of *d*-glyceric acid, see Frankland and P

Esters of *d*-diacetylglyceric acid were tested by Frank and MacGregor.[2]

See also the following papers:

Ethereal salts of active and inactive monobenzoyl-, dibenz diphenylacetyl-, and dipropionylglyceric acids.[3]

Effect of the mono-, di-, and trichloracetyl groups on rotatory power of methylic and ethylic glycerates and tartra

Frankland and Aston[5] give the following values for specific rotation of the methyl and ethyl esters of dito glyceric acid.

	$[\alpha]^{20}_D$	$[\alpha]^{100}_D$.
Methyl diparatoluyl glycerate	+ 41.21°	+ 25.09°
Ethyl diparatoluyl glycerate	+ 42.41	+ 26.18
Methyl dibenzoyl glycerate	+ 26.67	+ 17.43
Ethyl dibenzoyl glycerate	+ 26.08	+ 18.05
Methyl dimetatoluyl glycerate	+ 26.40	+ 16.45
Ethyl dimetatoluyl glycerate	+ 26.89	+ 17.40
Methyl diorthotoluyl glycerate	+ 20.19	+ 13.08
Ethyl diorthotoluyl glycerate	+ 21.64	+ 13.80

PHENYLDICHLORPROPIONIC ACID (cinnamic acid dichlorid $C_6H_5.CHCl—CHCl.CO_2H$. Resolved by aid of strychnine.

d-Acid, $[\alpha]_D = + 66.5°$.

Methyl ester: Alcohol	$[\alpha]_D$ =	+ 61.9°
Ethyl ester: Alcohol		+ 64.1

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[1] J Chem Soc., 71, 253

[2] *Ibid*, 63, 1419.

[3] Frankland and MacGregor *Ibid.*, 69, 104 (1896)

[4] Frankland and Patterson *Ibid.*, 73, 181 (1898)

[5] *Ibid*, , 75, 493 (1899).

l-Acid, $[\alpha]_D$ 65.9°.[1]

The following compounds may also find a place here:

(*l*?)-TYROSIN. $C_6H_4(OH)CH.NH_2.CO_2H$. Melting-point, 235° (Lippmann[2]); 290° (Erlenmeyer and Lippmann[3]).

Rotation in aqueous solution in presence of acid or alkali.

From silk:

21 per cent. HCl	*c*	4.51,	*t*	16.2°,	$[\alpha]_D$	7.98°[4]
11.6 per cent. KOH		5.8,		20.5,		9.01
11.6 per cent. KOH		11.51,		16.1,		8.86

From beet molasses:

21 per cent. HCl	*c*	3.92,	*t*	20°,	$[\alpha]_D$	8.07°[5]

From conglutin:

21 per cent. HCl	*c*	5,	$[\alpha]_D$	8.48°[6]
4 per cent. HCl		5,		15.6

A right-rotating tyrosin is known, $[\alpha]_D$ + 6.85,[7] but whether or not this is a position isomer has not been determined.

CYSTIN $(SC(CH_3)(NH_2)(COOH))$,

Dissolved in ammonia......	*p*	1.031,	$[\alpha]_D$	141.1°[8]
Dilute hydrochloric acid .	*c*	0.8 to 2,	$[\alpha]_D$	205.86°[9]
Dilute hydrochloric acid . .	*c*	2.13,	"	214°[10]

Derivatives

Bromphenylmercapturic Acid,

$CH_3.CONH.C(SC_6H_4Br)(CH_3).COOH$.

Alcohol	*p*	12 to 15,	$[\alpha]_D$	6.7°
Dilute NaOH .		25,		+ 6.4

Phenylmercapturic Acid, $CH_3CONH.C(SC_6H_5)(CH_3)COOH$.

Alcohol	*p*	20,	$[\alpha]_D$	9.3°

Na Salt, $CH_3CONH.C(SC_6H_5)(CH_3)COONa$.

Alkaline solution.....	*p*	8,	$[\alpha]_D$	+ 4.2°

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[1] Finkenbeiner: Ber. d. chem. Ges., 27, 880.

[2] *Ibid.*, 17, 2847.

Ann. Chem. (Liebig), 219, 173.

[4] Mauthner: Monatsh. Chem., 3, 343.

[5] Landolt: Ber. d. chem. Ges., 17, 2838.

[6] Schulze and Bosshard: Ztschr. physiol. Chem., 9, 98.

[7] Lippmann: Ber. d. chem. Ges., 17, 2839.

[8] Külz: Ztschr. für Biologie by Kühne and Voit, 20 [N. F. 2], 9.

[9] Mauthner: Ztschr. physiol. Chem., 7, 225.

[10] Baumann: *Ibid.*, 8, 305.

Bromphenylcysteïn, $(NH_2)(CH_3)C(SC_6H_4Br)COOH$.

Dilute NaOH .... $p = 9$, $[\alpha]_D = -3\,7^\circ$ [1]

10. Acids with Five Atoms of Oxygen

Malic Acids, $CO_2H\ CH.OH.CH_2.CO_2H$

NATURAL MALIC ACID, commonly known as *l*-malic aci This was first investigated by Pasteur[2] in aqueous solution found to be left rotating Later investigations by Schne. showed that the left rotation decreases with increasing centration, that inactivity is reached with $p = 34.24$, and then right rotation follows The dependence of the spe rotation on the percentage amount of water in the solutı is shown by the formula,

$$[\alpha]^{20}_D = 5\,891 - 0\,08959\,q \ (q = 30 \text{ to } 92),$$

which gives, for example, the following values :

q	p	$[\alpha]^{20}_D$	q	p	$[\alpha]^{20}_D$.
30	70	+ 3.203°	70	30	− 0.380°
40	60	+ 2.307	80	20	− 1 276
50	50	+ 1.412	90	10	− 2 172
60	40	+ 0.516	95	5	− 2 620

According to the above formula, the anhydrous malic ac must have the rotation, $[\alpha]_D = +\ 5\ 89$, and the substan must, therefore, be considered as right rotating. As shown §63, however, the right rotation may possibly depend on t formation of crystal molecules, and as the ordinary acid sho left rotation in other liquids besides water, acetone and meth alcohol for example, it is advisable to retain the old designatı of *l*-malic acid to avoid misunderstanding.

The right rotation of concentrated solutions is diminishe by increase of temperature, but the left rotation of dilute sol tions, on the other hand, is increased A solution with pe centage strength $p = 28.67$ is right rotating below 15°, bu left rotating above. For further details see §60.

On the rotation dispersion of malic acid see §46.

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[1] Baumann Ber d chem. Ges, **15**, 1731

[2] Ann chim phys, [3], **31**, 81

[3] Ann Chem. (Liebig), **207**, 261

For the rotation of solutions in acetone and methyl alcohol, Walden[1] found:

Acetone	$c = 13.3$,	$[\alpha]_D = -5.0$ to -5.34°
Methyl alcohol...	30,	-2.78

Influence of Sulphuric Acid and Acetic Acid on the Rotating Power of l-Malic Acid.—According to the experiments of Schneider,[2] the left rotation of dilute solutions of malic acid is decreased by addition of increasing amounts of the acids named, and after passing a point of inactivity, an increasing right rotation follows. The following figures were obtained, which are given in connection with the value of $[\alpha]_D$ for the pure aqueous solutions:

I SULPHURIC ACID.

Composition of the solutions in per cent by weight			Mol H_2SO_4 to 1 mol $C_4H_6O_5$ + 100 mol H_2O	Found $[\alpha]^{20}_D$.	$[\alpha]_D$ without H_2SO_4
$C_4H_6O_5$	H_2O	H_2SO_4.			
6.76	90.77	2.47	½	-1.33°	-2.46°
6.59	88.58	4.82	1	-0.76	-2.48
6.44	86.50	7.06	1½	-0.20	-2.49
6.29	84.51	9.20	2	$+0.21$	-2.50
6.15	82.61	11.24	2½	$+0.84$	-2.52

II ACETIC ACID.

Composition of the solutions in per cent by weight			Mol $C_2H_4O_2$ to 1 mol $C_4H_6O_5$ + 50 mol H_2O	Found $[\alpha]^{20}_D$.	$[\alpha]_D$ without $C_2H_4O_2$
$C_4H_6O_5$	H_2O	$C_2H_4O_2$			
10.04	67.47	22.49	5	-1.35°	-2.17°
8.20	55.08	36.72	10	-0.57	-2.33
6.00	40.29	53.71	20	$+0.13$	-2.53
5.29	35.52	59.19	25	$+0.14$	-2.59

Rotation without Addition of a Solvent.—From the formula of Schneider, above, which shows the dependence of the specific rotation of aqueous solutions of malic acid on the concentration, it follows that the acid must be right rotating in anhydrous condition, and show $[\alpha]_D = + 5.89°$ at a te perature of 20°

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[1] Ber. d. chem. Ges., **29**, 137

[2] Ann. Chem. (Liebig), **207**, 279

Walden[1] has been successful in observing this right rotat by rapidly melting the acid at a temperature of 100° to 11 and pouring it into a glass trough with parallel end surfac In the hot condition the liquid mass rotated to the left, l after cooling, the rotation was to the right. The followi rotations, referred to a layer 1 dm. in thickness, were found the Landolt ray filter method

	Temperature	
	90°–95°	17°
α for Red	− 4.4°	3.5°
Yellow (D)	− 5.5°	5.2°
Green	− 6.1°	6.8°
Light blue	− 7.0°	7.7°

The fused mass when dissolved in acetone exhibits le rotation, and the more strongly, the longer the heating wa continued ($[\alpha]_D = - 8°$ to $- 16°$). This shows the begi ning of anhydride formation

Alteration in the Acid on Heating.—As Walden[2] found, mali acid, when heated in the dry condition to 100° for twenty-fou hours, or when heated through a shorter time to 165° in vacuo is converted into a tribasic anhydro acid, $C_8H_{10}O_9$, while at a higher temperature (180°), a dibasic acid, $C_8H_8O_8$, is formed The two anhydrides show strong left rotation when dis solved in acetone, amounting to $[\alpha]_D = - 19$ to 25°, whil the original acid shows $[\alpha]_D = - 6°$ to $- 7°$.

Rotation of Malic Acid in Different Solvents.—Experiments on this point have been made by Nasini and Gennari[3] and also, especially, by Walden.[4] By help of ray filters, the latter found the following specific rotations, from which the corresponding dispersion coefficients, *Dc*, referred to $[\alpha]_D = 1$, were derived. All the values obtain for a temperature of 18°. As usual, *c* is the number of grams of malic acid in 100 cc. of solution

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[1] Ber d chem Ges, **32**, 2849 (1899)

[2] *Ibid*, **32**, 2706 (1899)

[3] Ztschr phys Chem., **19**, 117

[4] Ber d chem Ges, **32**, 2856 (1899)

It was found that the rotating power of *l*-malic acid is subject to extremely great variations.

Solvent	Benzyl alcohol		1 vol benzyl alcohol, 1 vol benzene.		3 vols benzyl alcohol, 2 vols. carbon disulphide	
c.	12.		6		4.8	
$[\alpha]$ Red	+ 2.7°	$Dc = 1$	+ 1.3°	$Dc = 1$	+ 1.8°	$Dc = 1$
Yellow *D*.	+ 4.0	1.5	+ 3.25	2.5	+ 3.4	1.9
Green ...	+ 5.5	2.0	+ 4.75	3.7	+ 4.4	2.5
Light blue	+ 7.7	2.85	+ 6.75	5.2	+ 6.5	3.6
Dark blue.	+ 11.0	4.1	+ 9.7	7.5	+ 8.5	4.8

In the above cases, the *l*-malic acid exhibits right rotation with strong rotation dispersion.

Solvent	Cryst formic acid		Acetone			
c	7.66	38.3	23.7 $t = 18°$		23.7 $t = 0°$	
$[\alpha]$ Red	− 3.7°	− 0.8°	− 5.0°	$Dc = 1$	− 4.6°	$Dc = 1$
Yellow *D*.	− 4.6	− 0.75	− 6.0	1.2	− 5.5	1.2
Green .	− 5.2	− 0.4	− 7.1	1.42	− 6.7	1.45
Light blue	− 5.9	+ 0.6	− 7.5	1.50	− 7.0	1.52

In these solvents, as in the following, the acid is left-rotating With formic acid the rotation decreases with the concentration and becomes even positive for the blue rays.

Solvent	3 vols acetone, 2 vols. benzene	Phenyl-methyl ketone	1 vol phenyl-methyl ketone, 1 vol paraldehyde.
c	9.44	5	5
$[\alpha]$ Red	− 4.0°	− 3.6°	− 3.0°
Yellow *D*.	− 4.1	− 4.0	− 3.0
Green ...	− 4.1	− 4.0	− 3.0
Light blue	− 4.2	− 4.6	− 3.0

In the above liquids we notice the very peculiar phenomenon that the rotation is nearly the same for all rays. The same behavior was observed by Nasini and Gennari for

aqueous solutions of malic acid having a concentrati
$c = 8.48$.[1]

Solvent.	1 vol acetone, 1 vol isobutyl alcohol				Isobutyl alcohol		1 vol fc acid, 1 vol acetat
c	11 8		5		10		9 58
		Dc.		*Dc*		*Dc*	
[α] Red	—5 8°	1	—6 2°	1	—3 2°	1	— 7.5°
Yellow *D*	—6 6	1.14	—6.3	1	—3.7	1 16	— 8 9
Green	—7 4	1 28	—8 4	1.35	—4 1	1 30	— 10.4
Light blue	—8.9	1 50	—8 5	1.37	—4 4	1 37	— 12 0
Dark blue.	....	....	—8 6	1 38	—5 0	1 56	..

In the above solutions the rotation increases but slig with the refrangibility of the rays; the rotation dispersio consequence is but weak.

Solvent	1 vol acetone, 1 vol paraldehyde		Acetaldehyde		Pyridine	
c	11 8		4		5	
[α] Red	—13 1°	*Dc* = 1	- 23 7°	*Dc* = 1	—23 0°	*Dc* = 1
Yellow *D*.	—17 6	1 35	—28 7	1.21	—30 0	1
Green	—22.9	1.75	—32 5	1.33	—36 0	1
Light blue	—27.5	2.10	—38.7	1 63	...	.

These three liquids which are able to act chemically on t malic acid produce a very strong increase in the left rotatio while the dispersion is not greatly increased.

A substance which has the power of enormously increasin the activity of malic acid is, as Walden[2] observed, urany nitrate with simultaneous addition of alkali. The specifi rotation with this addition may be increased to 158 times tha shown by a pure aqueous solution of the acid of the same concentration. It is probable that the high rotation correspond to the alkali salt of a complex uranyl malic acid. Walden ha investigated the following ten mixtures of different compositions, in which it is seen that the maximum of rotation is found in solutions Nos. 6 and 7. These correspond to a relation of 1 mol of malic acid, 4 mols. of potassium hydroxide, and 1 to 4 mols. of uranyl nitrate, $UO_2(NO_3)_2 + 6H_2O$.

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[1] *Loc cit.*

[2] Ber. d chem Ges, 30, 2889 (1897)

No	In 100 cc aqueous solution			α_D 2 dm	$[\alpha]_D$
	Malic acid Grams.	Potassium hydroxide Grams	Uranyl nitrate, Grams		
1	0.65	1.08	..	—0.04°	— 3°
2	0.65	....	10	—0.14	— 11
3	0.65	0.27	2	—1.80	—139
4	0.65	0.54	2	—3.60	—277
5	0.65	0.54	10	—3.13	—241
6	0.65	1.08	3	—6.17	—475
7	0.65	1.08	10	—6.09	—470
8	0.65	1.08	20	—5.81	—447
9	0.65	1.08	34	—5.43	—415
10	0.65	1.62	10	—5.86	—451

By uranyl acetate, with addition of alkali, the rotation not only of malic acid, but also that of *d*-tartaric acid, *d*-methyl tartrate, *l*-quinic acid, and *l*-mandelic acid is greatly increased, and with preservation of the direction of rotation of aqueous solutions of these substances On the other hand, uranyl acetate produces no increase in activity in *d*-chlorsuccinic acid, *l*-bromsuccinic acid, and *d*-amyl acetic acid. The action appears, therefore, only when the acids possess a free hydroxyl group.[1]

Salts of l-Malic Acid

The specific rotation of aqueous solutions of these has been investigated by G. Schneider.[2] He gives the following formulas for the relation of the specific rotation to the percentage content of water q holding for the temperature of 20°

$KH\,C_4H_4O_5$ $q = 73–90$, $[\alpha]_D = -0.6325 - 0.05562\,q$
K_2 " $38–90$, $= 3.016 - 0.1588\,q + 0.0005555\,q^2$
NaH " $39–80$, $= 9.367 - 0.2791\,q + 0.001152\,q^2$
Na_2 " $34–94$, $= 15.202 - 0.3322\,q + 0.0008184\,q^2$
$LiH.$ " $50–90$, $= 8.572 - 0.3573\,q + 0.001868\,q^2$
Li_2 " $60–94$, $= 26.717 - 0.6821\,q + 0.002878\,q^2$
$NH_4H.$ " $72–94$, $= -3.955 - 0.02879\,q$
$(NH_4)_2$ " $37–83$, $= -3.315 - 0.005042\,q - 0.0005115\,q^2$

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[1] Walden Ber. d. chem. Ges., **30**, 2889 (1897).

[2] Ann. Chem (Liebig), **207**, 266 to 277.

The specific rotations for a number of solutions are accordingly:

p	q.	KH	K_2	NaH.	Na_2	LiH	Li_2	NH_4H	$(NH_4)_2$
60	40	...	− 2.45°	+ 0.05°	+ 3.22°	....	....	....	− 4.34°
50	50	...	− 3.59	− 1.71	+ 0.64	− 4.62°	....	....	− 4.85
40	60	..	− 4.51	− 3.23	− 1.78	− 6.14	− 3.85°	...	− 5.46
30	70	− 4.53°	− 5.38	− 4.53	− 4.04	− 7.29	− 6.93	− 5.97°	− 6.17
20	80	− 5.08	− 6.13	− 5.59	− 6.14	− 8.06	− 9.43	− 6.26	− 6.99
10	90	− 5.64	− 6.78	....	− 8.07	− 8.45	−11.36	− 6.55	....

On the inactivity point in the concentration, see §57.[1]

For dilute solutions of salts of malic acid see §61.

A series of observations on the specific rotation of neutral sodium malate has been carried out by Th. Thomsen.[2] According to these experiments the point of inactivity is found for a strength of 45.63 per cent. of the salt

Through the presence of free alkalies, the rotation of the malates is displaced in the direction, left to right, that is, the action follows in the same direction as with addition of free acids. The following experiments by Thomsen[3] show the extent of the change

p	$[\alpha]_D^{20}$		Amount of change
	Of the pure $Na_2C_4H_4O_5$	After addition of 1 mol NaOH to 1 mol salt	
28.93	− 4.02°	+ 0.37°	4.39°
19.23	− 6.31	− 4.05	2.26
10.94	− 7.90[4]	− 6.56	1.34

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[1] In using the interpolation formula with three constants, the composition of the solution with which inactivity must appear, is most easily found by bringing the equation $A - Bq + Cq^2 = 0$ into the form $q^2 + \frac{Bq}{C} = -\frac{A}{C}$, and then applying the two trigonometric formulas

1. $$2\frac{C}{B}\sqrt{\frac{A}{C}} = \sin a,$$

2. $$q = \tan\frac{a}{2}\sqrt{\frac{A}{C}}$$

[2] J. prakt. Chem., [2], 35, 153

[3] *Loc cit*

[4] Calculated from Schneider's formula

p	$[\alpha]^{20}_D$ Of the pure $Na_2C_4H_4O_5$	$[\alpha]^{20}_D$ After addition of 3 mol NaOH to 1 mol salt	Amount of change
27.23	− 4.84°	+ 10.74°	15.58°
18.71	− 6.39	+ 1.99	8.38
9.38	− 8.19[1]	− 5.09	3.10

The alteration increases, therefore, with the amount of free alkali added, and is the greater the stronger the solution is. Solutions which are originally left rotating become in this way, easily, right rotating.

The influence of temperature on the specific rotation of the malates is shown, as with the free acid, in displacing the rotation in the direction right to left for increase in temperature. Th Thomsen[2] has noted the change for the following salts:

	$K_2C_4H_4O_5$				$Na_2C_4H_4O_5$		
	$[\alpha]_D$ at				$[\alpha]_D$ at		
p	10°	20°	30°	p	10°	20°	30°
33.86	− 4.48°	− 5.22°	− 5.85°	42.75	+ 0.38°	− 0.89°	− 2.04°
23.25	− 5.18	− 5.90	− 6.57	28.60	− 3.41	− 4.52	− 5.58
16.29	− 5.62	− 6.35	− 7.09	19.51	− 5.30	− 6.36	− 7.41
.	.	..	.	14.46	− 5.98	− 7.07	− 7.96

Barium Malate, $BaC_4H_4O_5$

p =	9.383	8.505	4.994	1.965
$[\alpha]^{20}_D$ =	+ 8.18°	+ 8.05°	+ 4.69°	− 2.58°

This salt is, therefore, right-rotating down to a strength of the solutions of about 3 per cent.[3]

Ammonium-Antimonyl Malate, $NH_4SbOC_4H_4O_5$, shows a very high specific rotation to the right

Water.. $p = 6.845$, $t = 17°$, $[\alpha]_j = + 115.47$, $[\alpha]_D = + 102.64.°$[4]

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[1] Calculated from Schneider's formula

[2] Ber d chem Ges, **15**, 443

[3] Schneider Ann Chem (Liebig), **207**, 277

[4] Pasteur Ann chim phys, [3] **31**, 85

For the action of alkali molybdates and tungstates on l acid, see §70, p. 250.

Esters of l-Malic Acid

Walden[1] gives the following constants for the derivativ ordinary malic acid :

	Boiling-point	mm	d_4^{20}.	[α
Dimethyl malate	125°	10	1 2337	—
Diethyl "	149	25	1 1294	— 1
Dipropyl "	152	10	1 4380	— 1
Diisopropyl "	147	14	1 0760	— 1
Diisobutyl "	175	15	1 0418	— 1
Di-*l*-amyl "	191–192	20	1 0176	— 6
Di-*i*-amyl "	191–192	20	1.0179	— 9
Dicapryl "	230	20	0 9761	— 6
Dimethyl acetylmalate	157	35	1 1975	— 22
Diethyl "	145	10	1 1168	— 22
Dipropyl "	162–163	16	1 0724	— 22
Diisobutyl "	179	20	1 0362	— 21.
Dimethyl propionylmalate	145–147	8	1 1609	— 22
Diethyl "	150	9	1 0958	— 22
Dimethyl *n*-butyrylmalate	150	10	1 1317	— 22
Diethyl "	162–163	12	1 0736	— 22
Dipropyl "	174–175	16	1 0417	— 22
Diisobutyl "	190–192	14	1 0146	- 21
Dimethyl isobutyrylmalate	140	8	1 1255	— 22
Diethyl "	160	15	1 0688	- 21
Dimethyl isovalerylmalate	158–160	10	1 1034	— 22
Diethyl "	168	10	1 0605	— 22
Dipropyl "	182–183	17	1 0263	— 21 6
Diisobutyl "	195	16	1 0045	- 19 9
Dimethyl chloracetylmalate	187–188	37	1 3062	— 23 3
Dipropyl "	182–184	15	1 1566	- 23 5
Dimethyl bromacetylmalate	194–195	22	1 5072	- 22 4
Diethyl "	178–182	10	1 3936	— 22 4
Dipropyl "	192–193	17	1 3150	— 22 2
Diisobutyl "	195–197	15	1 2022	— 20 3
Diethyl α-brompropionylmalate	187–188	12	1 3325	— 22 4
Diethyl α-brombutyrylmalate	188–190	10	1.3059	— 24 7
Diethyl α-bromisobutyrylmalate	177–180	12	1 2850	— 22.5
Dimethyl nitromalate	(Chloroform, $c = 4$ 0)			— 18 8
Malic acid diamide	m p 156–158, water,		$c = 4$ 32	— 37 6
" " "	" " "		$c = 8$ 65	— 38.0
" " dianilide	" 196 $C_2H_4O_2$		$c = 1$ 50	— 60 66
" " "	m. p 196 " "		$c = 0$ 750	— 58.66
" " di-*o*-toluide	" 181 " "		$c = 2.00$	— 65 0
" " "	" " " "		$c = 1$ 00	— 66.5
" " di-*p*-toluide	" 207 " "		$c = 1.00$	— 70 0
" " β-naphtimide	" 193–195 " "		$c = 1.00$	— 51 5

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[1] Walden Ztschr phys Chem , 17, 248

Anschütz and Reitter[1] find.

	Boiling-point at 12 mm	d^{20}_4.	$[\alpha]_D$.
Methyl malate	122°	1.2334	— 6.88°
Ethyl "	129.2–129.6	1.1280	— 10.55
n-Propyl "	150	1.0736	— 11.60
n-Butyl "	169.4–170.4	1.0382	— 10.72
Methyl acetylmalate	131.8–132	1.1983	— 22.86
Ethyl "	141.2–141.4	1.1169	— 22.60
n-Propyl "	158.6–159.2	1.0729	— 22.68
n-Butyl "	177.4–178.2	1.0430	— 19.93

Purdie and Williamson[2] have obtained nearly the same results for some of these esters.

Frankland and Wharton[3] have made the following determinations:

	Bp	mm	d^t_4	t	$[\alpha]^t_D$.
Methyl benzoyl malate	210–223°	12	1.2121	21°	– 5.62°
Ethyl " "	210–220	12	1.1561	21	— 3.87
Methyl orthotoluyl malate	214–225	12	1.1909	23	— 8.94
Ethyl " "	215–225	12	1.1391	21	— 6.25
Methyl metatoluyl malate	215–225	12	1.1925	20	— 6.34
Ethyl " "	212–220	13	1.1371	21	— 4.67
Methyl paratoluyl malate	200–225	13	1.1957	18.5	— 3.14
Ethyl " "		.	1.1382	20	— 0.22

The densities and rotations were determined for a wide range of temperatures and the latter were found to vary greatly with the temperature.

d-MALIC ACID. Antimalic acid.

By reduction of *d*-tartaric acid or by resolution of the *r*-malic acid from racemic acid by aid of cinchonine.[4] Also from *d*-asparagin by action of nitrous acid.[5]

d-Ammonium Hydromalate.

Water....... $p = 8$, $[\alpha]_D = + 6.3$ (*l*-salt $[\alpha]_D = - 6.2$)[6]

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[1] Ztschr. phys. Chem., **16**, 493.

[2] J. Chem. Soc., **69**, 830.

[3] *Ibid.*, **75**, 337.

[4] Bremer: Ber. d. chem. Ges., **8**, 1594; **13**, 351.

[5] Piutti: *Ibid.*, **19**, 1693.

[6] Bremer: *Loc. cit.*

d-Malic acid, from *d*-chlorsuccinic acid, shows according t Walden.[1]

Acetone	$c = 16$,	$[\alpha]_D = +5.2°$
Methyl alcohol	$c = 30$,	" $= +2.92$

d-METHOXYSUCCINIC ACID, $CO_2H.CH(O.CH_3).CH_2.CO_2H$ Crystals, melting-point 88° to 90°. By cinchonine resolution of the *r*-acid obtained by addition of methyl alcohol t fumaric acid,[2] or by strychnine resolution.[3]

Water	$c = 11.208$,	$t = 18°$,	$[\alpha]_D = +33.30°$	[4]
"	$c = 5.586$,	$t = 18°$,	" $= +33.04$	
"	$c = 24.65$,	$t = 15°$,	" $= +32.59$	[5]
"	$c = 16.08$,	$t = 14°$,	" $= +32.79$	
"	$c = 8.76$,	$t = 15°$,	" $= +32.70$	
Acetone	$c = 24.96$,	$t = 11°$,	" $= +57.10$	
"	$c = 18.77$,	$t = 11°$,	" $= +58.29$	
"	$c = 10.30$,	$t = 14°$,	" $= +58.03$	
"	$c = 4.12$,	$t = 14°$,	" $= +59.49$	
"	$c = 1.65$,	$t = 14°$,	" $= +60.09$	
Ethyl acetate	$c = 20.54$,	$t = 11°$,	" $= +63.48$	
" "	$c = 15.87$,	$t = 12°$,	" $= +64.45$	
" "	$c = 8.92$,	$t = 12°$,	" $= +64.64$	

Salts.—In the following data by Purdie and Marshall, the concentrations refer to the anhydrous salts:

Acid Potassium Salt, crystalline.[6]

Water	$c = 4.010$,	$t = 18.5°$,	$[\alpha]_D = +23.46°$
"	$c = 8.150$,	$t = 18°$,	" $= +23.26$

Normal Potassium Salt, crystalline.[6]

Water	$c = 5.019$,	$t = 14.5°$,	$[\alpha]_D = +9.36°$
"	$c = 12.162$,	$t = 15.5°$,	" $= +9.54$

Acid Ammonium Salt, crystalline.[6]

Water	$c = 6.064$,	$t = 14°$,	$[\alpha]_D = +25.86°$

Normal Ammonium Salt, crystalline.[6]

Water	$c = 2.823$,	$t = 14°$,	$[\alpha]_D = +12.22°$
"	$c = 5.762$,	$t = 14°$,	" $= +12.32$

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[1] Ber. d. chem. Ges., **29**, 137.
[2] Purdie and Marshall. J. Chem. Soc., **63**, 217.
[3] Purdie and Bolam. *Ibid.*, **67**, 946.
[4] Purdie and Marshall.
[5] Purdie and Bolam.
[6] Purdie and Marshall.

Calcium Salt, crystalline.[1]

Water.......... $c = 5.308$, $t = 18°$, $[\alpha]_D = -10.10°$

Barium Salt, $C_5H_6O_5.Ba + \frac{1}{2}H_2O$, crystalline [1]

Water, $c = 26.125$ (anhydrous), $t = 18°$, $[\alpha]_D = -14.27°$
" $c = 12.416$ " $t = 18°$, " $= -7.36$
" $c = 5.746$ " $t = 18°$, " $= -2.21$
" $c = 1.149$ " $t = 18°$, " $= +3.16$

Cinchonine Salt, $C_5H_8O_5.C_{19}H_{22}N_2O$ Crystals, melting-point 171° to 173°.[1]

Water .... $c = 4$, $t = 17°$, $[\alpha]_D = +154.89°$

Methyl Ester, $d_4^{12} = 1.1498$, $[\alpha]_D = +52.51$.[2]

l-METHOXYSUCCINIC ACID Crystals, melting-point 89°.

Water.......... $c = 10.806$, $t = 18°$, $[\alpha]_D = -32.94°$ [1]
" .... $c = 22.035$, $t = 15°$, " $= -32.70$ [3]
" .... $c = 7.927$, $t = 15°$, " $= -32.42$
Acetone........ $c = 25.588$, $t = 11°$, " $= -56.25$
" .... $c = 15.614$, $t = 13°$, " $= -58.18$
Ethyl acetate... $c = 25.511$, $t = 11°$, " $= -61.90$
" " .. $c = 19.077$, $t = 13°$, " $= -62.93$

Salts,[1]

Acid Potassium Salt, crystalline.

Water...... $c = 4.046$, $t = 18°$, $[\alpha]_D = -23.59°$
" .... $c = 4.083$, $t = 17.5$, " $= -23.49$

Acid Ammonium Salt, crystalline

Water.......... $c = 8.774$, $t = 18°$, $[\alpha]_D = -25.85°$

Calcium Salt, crystalline.

Water .. $c = 5.482$, $t = 13°$, $[\alpha]_D = +10.03°$
" .... $c = 2.210$, $t = 14.5$, " $= +4.30$

Some esters have been investigated by Purdie and Williamson.[4]

Ethyl ester............ $d_4^{18} = 1.0705$, $[\alpha]_D = -50.11°$
Propyl ester.............. $d_4^{15} = 1.0419$, " $= -45.21$
N-Butyl ester ...... $d_4^{15} = 1.0419$, " $= -41.63$

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[1] Purdie and Marshall.

[2] Purdie and Williamson. J. Chem. Soc., **67**, 971

[3] Purdie and Bolam

[4] J Chem. Soc., **67**, 971

d-ETHOXYSUCCINIC ACID, $CO_2H.CH(O.C_2H_5).CH_2.CC$

By resolution of the *r*-acid by *Penicillium glaucum*,[1] or strychnine[2] Crystals, melting-point 76° to 80°.

Water ..... $c = 11.17$, $t = 17°$, $[\alpha]_D = +33.02°$
" .... $c = 5.56$, $t = 19$, " $= +32.54$
" ...... $c = 8\text{–}22.5$, $t = 12\text{–}17$, " $= +34.4\text{–}34.7$
Chloroform .. $c = 11.61$, $t = 12$, " $= +47.75$
" .. $c = 4.80$, $t = 12$, " $= +45.55$
" .. $c = 4.52$, $t = 11$, " $= +44.17$
" .. $c = 1.60$, $t = 11$, " $= +39.40$
Ethyl alcohol $c = 11.81$, $t = 11$, " $= +60.57$
Ethyl acetate $c = 5\text{–}20$, $t = 18$, " $= +69.9\text{–}70.5$
Acetone ..... $c = 9.57$, $t = 14$, " $= -63.39$
" .... $c = 3.83$, $t = 14$, " $= -64.87$
" ..... $c = 1.53$, $t = 14$, " $= -66.48$

Salts.[3]

Acid Potassium Salt, $KC_6H_9O_5 + H_2O$, crystalline. Melting point 160°

Water ... . $c = 3.93$ (contains water), $t = 19°$, $[\alpha]_D = +26.4$

Acid Ammonium Salt, $NH_4C_6H_9O_5 + H_2O$, crystalline.[1]

Water .. .... $c = 8.13$ (contains water), $t = 15°$, $[\alpha]_D = +28.6$
" .. .. . $c = 4.59$ " " $t = 16$, " $= +29.0$
" . .. . . $c = 2.58$ " " $t = 17$, " $= +28.4$

Normal Ammonium Salt, $(NH_4)_2C_6H_8O_5$, crystalline

Water .... $c = 5.22$ (anhydrous), $t = 14.5°$, $[\alpha]_D = +18.29$
" .... $c = 1.48$ " $t = 12$, " $= +18.93$

Calcium Salt, $CaC_6H_8O_5$, crystalline.

Water. .. . . . $c = 3.04$, $t = 15°$, $[\alpha]_D = +8.39°$
" .... $c = 1.79$, $t = 15$, " $= +11.44$

Barium Salt, $BaC_6H_8O_5$ (at 160°), crystalline

Water .... $c = 4.56$, $t = 18°$, $[\alpha]_D = +6.37°$
" ... . $c = 10.77$, $t = 18$, " $= +2.46$
" . .. . $c = 25.08$, $t = 19$, " $= -4.37$

Esters.[5]

Methyl ester.... . .... . $d_4^{13} = 1.1055$, $[\alpha]_D = +59.86°$
Ethyl ester.... .... $d_4^{17} = 1.0418$, " $= +55.29$

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[1] Purdie and Walker J Chem Soc, **63**, 229

[2] Purdie and Williamson *Ibid*., **67**, 963

[3] Purdie and Walker *Loc. cit*

[4] Purdie and Walker

[5] Purdie and Williamson J Chem Soc, **67**, 971

l-ETHOXYSUCCINIC ACID Solutions in water.[1]

Acid ammonium salt....	$p = 2.5$	$[\alpha]_D = -26.05°$	[2]
Methyl ester	$d_4^{20} = 1.0996$,	" $= -60.92$	[3]
Propyl ester	$d_4^{7} = 1.0226$,	" $= -51.20$	
N-Butyl ester..........	$d_4^{6} = 1.0045$,	" $= -46.43$	
Ethyl ester.............	$d_4^{20} = 1.1045$,	" $= -1.44$	[4]

Ethyl Ethoxysuccinate. See Purdie and Pitkeathly.[5]

PROPOXYSUCCINIC ACIDS, $CO_2H.CH(O\,C_3H_7).CH_2.CO_2H$.[6]

d-Acid.	Water........	$c = 7.56$,	$t = 12°$,	$[\alpha]_D = +36.04°$
d-Acid, potassium salt..		$c = 3.815$,	$t = 18$,	" $= +32.30$
d-Normal salt		$c = 3.665$,	$t = 18$,	" $= +17.26$
" "		$c = 1.833$,	$t = 18$,	" $= +18.69$
l-Acid	Water	$c = 7.760$,	$t = 12$,	" $= -36.40$
"	"	$c = 3.104$,	$t = 12$,	" $= -36.24$
l- Acid.	Acetone	$c = 5.688$,	$t = 12$,	" $= -63.29$
"	" . .	$c = 2.275$,	$t = 12$,	" $= -64.39$
l-Barium salt	Water..	$c = 3.649$,	$t = 18$,	" $= -10.00$
" "	" .	$c = 1.460$,	$t = 18$,	" $= -10.45$

Propyl Propoxysuccinate. For the preparation and optical behavior of this ester see Purdie and Lander.[7]

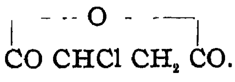
d-CHLORSUCCINIC ACID, $CO_2H\,CHCl.CH_2.CO_2H$

From ordinary malic acid by action of phosphorus pentachloride Melting-point 174°

1. Water . . . . $t = 21°$, c = 16 6.4 3.2
$[\alpha]_D = +20.6$ $+20.8$ $+21.3°$[8]

2. Water.......	$c = 6.66$	"	$+20.27$	[9]
Ethyl acetate.	$c = 10$	"	$= +52.70$	
" "	$c = 6.66$	"	$= +52.85$	

Derivatives



Anhydride, $\overbrace{\mathrm{CO\ CHCl\ CH_2\ CO}}^{\mathrm{O}}$. Melting-point 80°.

Ethyl acetate	$c = 10$,	$[\alpha]_D = +30.85$	[9]
" "	$c = 5$,	" $= +33.60$	

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[1] Purdie and Walker · J Chem Soc, **63**, 238

[2] Purdie and Walker,

[3] Purdie and Williamson J. Chem Soc., **67**, 972

[4] Walden Ztschr phys. Chem., **17**, 252

[5] J. Chem Soc, **75**, 157

[6] Purdie and Bolam, J Chem Soc, **67**, 949

[7] J. Chem. Soc., **73**, 288 (1898)

[8] Walden: Ber. d chem Ges., **26**, 225.

[9] Walden. Ztschr. phys Chem, **17**, 253.

Chloride, COCl.CHCl.CH_2.COCl. Boiling-point 91° t (11 mm.), $d_4^{20} = 1.5002$, $[\alpha]_D = + 29.53$.[1]

Dimethyl ester..	B p. 114-115	(17 mm),	$d_4^{20} = 1.2555$,	$[\alpha]_D = + 4$
Diethyl ester. ..	" 130-131	(20 "),	" = 1.1493,	" = + 2
Dipropyl ester...	" 148	(20 "),	" = 1 0925,	" = + 2
Diisobutyl ester.	" 162-164	(17 "),	" = 1.0524,	" = + 21
Diamyl ester....	" 190	(25 "),	" = 1 0319,	" = + 21

l-CHLORSUCCINIC ACID. By action of nitrosyl chlorid *l*-asparagin Melting-point 174°.[3]

Water .... $c = 9.3$, $t = 19°$, $[\alpha]_D = - 19.67°$.

d-BROMSUCCINIC ACID, $CO_2H.CHBr.CH_2.CO_2H$.

From ordinary malic acid and phosphorus pentabromide

Dimethyl ester...	B. p. 129	(23 mm.),	$d =$? ,	$[\alpha]_D = + 50.$
Diethyl ester .	" 143	(29 "),	$d =$? ,	" = + 40
Dipropyl ester ..	" 153-154	(18 mm.),	$d = 1\ 3010$,	" = + 38.

l-BROMSUCCINIC ACID By action of nitrosyl bromide *l*-asparagin Melting-point 173°.[7]

Ether....	$c = 5\ 33$,	$[\alpha]_D = - 67\ 92°$
Ethyl acetate.....	$c = 6\ 66$ to $5\ 33$,	$= - 72.7$ to $72\ 6$

Monamide, $CO_2H.CHBr.CH_2.CONH_2$.

Alcohol..	$c = 6\ 66$,	$[\alpha]_D = - 67\ 12°$
Ethyl acetate	$c = 6\ 66$,	" $= - 67\ 57$
20 per cent aqueous H_2SO_4.. .	$c = 3\ 00$,	" $= - 44\ 3$

d-ASPARTIC ACID, $CO_2H.CH_2\ CHNH_2.CO_2H$. From asparagin. In hydrochloric acid solution, left rotating.

l-ASPARTIC ACID. Ordinary acid. From *l*-asparagin

1. Solutions in water are right rotating at the ordinary ten perature, at 75° inactive, and above that, increasingly le rotating.[8] See §60 For $t = 20°$ and $c = 0.5°$, $[\alpha]_D = -$ 4.36°. Stated earlier by Becker[9] to be left rotating.

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[1] Walden *Loc cit*

[2] Walden *Loc cit*, and Ber d chem Ges, **28**, 1289

[3] Tilden and Marshall. J Chem Soc., **67**, 494

[4] Walden Ber d chem Ges, **28**, 1290

[5] Walden · *Loc. cit*

[6] Walden · Ztschr. phys Chem, **17**, 254

[7] Walden · Ber d. chem Ges, **28**, 2769

[8] Cook *Ibid*, **30**, 204

[9] *Ibid*, **14**, 1035

2. Solutions in aqueous acids exhibit right rotation.[1] Becker[2] investigated the following solutions which contained :

FOR 1 MOL. OF ASPARTIC ACID.

1 54 to 64 mol. water + n mol HCl	$[\alpha]_D$	2 302 mol water + n mol. H_2SO_4.	$[\alpha]_D$
$n = 1$	+ 30.0°	$n = 0.5$	+ 21.8°
1.5	+ 32.6	0.6	+ 24.2
2	+ 33.4	0.75	+ 28.6
3	+ 34.0	1	+ 28.8
5	+ 33.9	3	+ 31.5
6	+ 34.0	5	+ 32.0
..	....	10	+ 33.5

3. Solutions in aqueous alkalies are left rotating.[3] Becker[4] found for solutions which for one molecule of aspartic acid contained :

a 277 to 285 mol water, 1 to 3 mol. NaOH $\}$ $[\alpha]^{20}_D = -9.07$ to $9.04°$

b 302 mol water + 1 mol. NH_3 $[\alpha]^{20}_D = -9.2°$
" " " + 3 " " " $= -9.4$
" " " + 5 " " " $= -9.5$
" " " + 15.1 " " " $= -11.1$
" " " + 20.2 " " " $= -12.1$

d-β-ASPARAGIN, $CONH_2.CH_2.CHNH_2.CO_2H$.

For formation see Bischoff and Walden.[5]

Water....... . $[\alpha]_D = +5.41$ (*l*-Asparagin $= -5.43$)[6]

l-β-ASPARAGIN. Ordinary asparagin.

In aqueous and alkaline solutions, left rotating, in acid solutions right rotating.[7]

The following determinations were all made by Becker.[8]

a. Solutions in water :

p	d^{20}_4	$[\alpha]^{20}_D$
$p = 0.705$	$d^{20}_4 = 1.0010$	$[\alpha]^{20}_D = -5.95$
1.049	1.0025	− 5.42
1.409	1.0043	− 5.30

---

[1] Pasteur: Ann. chim. phys., [3], 31, 81; 34, 30.
[2] Ber. d. chem. Ges., 14, 1038.
[3] Pasteur: *Loc. cit.*
[4] Ber. d. chem. Ges., 14, 1037.
[5] "Handb. d. Stereochemie," 1894, p. 220.
[6] Piutti: Ber. d. chem. Ges., 19, 1693.
[7] Pasteur: Ann. chim. phys., [3], 31, 75.
[8] Ber. d. chem. Ges., 14, 1030.

b. Solutions in dilute acids .

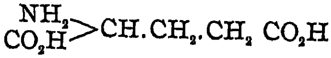
TO 1 MOL ASPARAGIN + 300 MOL. WATER

Mol HCl	$[\alpha]_D^{20}$.	Mol H_2SO_4.	$[\alpha]_D^{20}$.	Mol $C_2H_4O_2$	$[\alpha]_D^{20}$.
1	+ 26 4	0 5	+ 23 1	1	− 3.49
1 5	+ 30 4	0 75	+ 27 3	2	− 3.10
2	+ 31 5	1	+ 29 5	5	− 1.45
3	+ 31 9	3	+ 32 0	7	− 0.59
5	+ 32 3	5	+ 34 3	10	0.00
10	+ 33 3	10	+ 35.5	15	+ 1.11
15	+ 33 7	..	....	20	+ 2.63
20	+ 34 3	.	. ..	..	....

While hydrochloric and sulphuric acids produce strong right rotation, small amounts of acetic acid produce left rotation. This last decreases with added acid and is finally changed to right rotation. That the addition of acetic acid under certain conditions of concentration may cause the rotating power of asparagin to disappear was noticed by Champion and Pellet.[1]

c. Solutions in dilute sodium hydroxide.

In 100 parts of solution			Mol. proportions			d_4^{20}	$[\alpha]_D^{20}$.
Asparagin	NaOH.	H_2O	Asparagin	NaOH	H_2O		
10	3	87 0	1	1	63.8	1 0584	− 8 64
10	6 1	83 9	1	2	61 5	1 0915	− 6 69
10	9 1	80 9	1	3	59 3	1.1232	− 6 35

d-GLUTAMINIC ACID, 
$\begin{matrix} NH_2 \\ CO_2H \end{matrix}>CH.CH_2.CH_2\ CO_2H$

Water ... . $c = 2$, $t = 21°$, $[\alpha]_D = + 10.2°$
" .... $c = 4$ (supersaturated), $t = 23$, " $= + 10.6$
Dil nitric acid.... $c = 4$, $t = 22$, " $= + 29.9$

Calcium Salt, $CaC_5H_7NO_4$ Left rotating.

Water....... .... .. $c = 5$ 03, $t = 20°$, $[\alpha]_D = - 3.7°$

Hydrochloride, $C_5H_9NO_4.HCl$.

Water .... $c = 4$, $t = 21°$, $[\alpha]_D = + 20.4°$[2]

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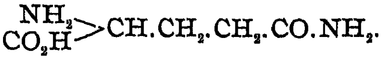
[1] Compt rend, 82, 819

[2] Scheibler Ber d. chem, Ges, 17, 1728

l-GLUTAMINIC ACID. From the racemic acid by means of *Penicillium glaucum* In 100 cc. 9 grams. HCl + 5 grams glutaminic acid, $[\alpha]_D = -31.1$.[1]

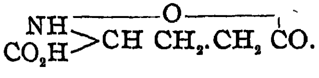
d-GLUTAMINE,



$\genfrac{}{}{0pt}{}{NH_2}{CO_2H}{>}CH.CH_2.CH_2.CO.NH_2.$

In 100 cc. 0.45 grams H_2SO_4 + 5 grams glutamine, $[\alpha]_j = +30.0$[2]
" 100 " 0.3 " $H_2C_2O_4$ + 2.7 " " " $= +18.3$

d-PYROGLUTAMINIC ACID,



$\genfrac{}{}{0pt}{}{NH}{CO_2H}{>}CH\;\overbrace{CH_2.CH_2\,CO}^{O}.$

Water . . . . $c = 2.665$, $t = 25°$, $[\alpha]_D = +7°$[3]
l-Acid . . . . $[\alpha]_D = -6.1$[4]

SHIKIMIC ACID, $C_7H_{10}O_5$. Cyclic. Needles. Melting-point 184°. The following observations were made by Eykman.[5]

Water . . .	$c = 36.26$,	$[\alpha]^{19}_D = -204.4°$,	$c = 11.19$,	$[\alpha]^{19}_D = -187.9°$
	30.73,	-201.5,	7.53	-186.7
	21.71,	-195.5,	5.93	-184.7
	13.12,	-190.0,	4.03	-183.8

From which is calculated $[\alpha]_D = -183.3 - 0.65\,c$

Solutions in acetic acid, and especially in 50 per cent. sulphuric acid, exhibit increasing rotation ; but tellurous acid decreases the rotation in marked degree, while selenous acid leaves it unchanged.

Ammonium Salt, $(NH_4)C_7H_9O_5$. Rhombic prisms

Water	$c = 32.00$,	$[\alpha]_D = -189.7°$
	5.23,	-172.1

Triacetylshikimic Acid, $C_7H_7O_5(C_2H_3O)_3$. Amorphous.

Absolute alcohol	$c = 5.496$,	$[\alpha]_D = -170.0°$
" "	3.482,	-169.6
" "	1.451,	-170.2
Benzene	7.255,	-191.1
"	4.230,	-191.7
"	2.392,	-192.1
Chloroform	3.482,	-189.7
"	4.222,	-189.2

---

[1] Schulze and Bosshard Ztschr physiol. Chem., 10, 143
[2] Schulze and Bosshard · Ber d chem Ges., 18, 390
[3] Menozzi, Appiani Rend Acc Linc., 1893, II, 421
[4] Menozzi, Appiani . Gaz chim ital., 22, II, 105
[5] Ber d. chem Ges., 24, 1278

Tripropionylshikimic Acid, $C_7H_7O_5(C_3H_5O)_3$. Amor

Absolute alcohol .... $c = 7\ 361$, $[\alpha]_D = -159.1$
" " .... $3\ 680$, -159.0
Benzene .... 7.125, -172.8
" .... $5\ 360$, -173.3

Triisobutyrylshikimic Acid, $C_7H_7O_5(C_4H_7O)_3$. Amor

Absolute alcohol .... $c = 9.314$, $[\alpha]_D = -146.1°$
Benzene .... $7\ 247$, $-157\ 9$

Shikimic Acid Bromide, $C_7H_9BrO_5$. Hemimorphous, agonal needles Melting-point 235° (uncorr.).

Water .... $c = 8$, $[\alpha]_D = +22°$

Hydroshikimic Acid, $C_7H_{12}O_5$. Monosymmetric pr Melting-point 175° (uncorr.).

Water . $p = 16.515$, $d^{23} = 1.054$, $t = 23°$, $[\alpha]_D = -35\ 8°$

After dilution with an equal volume of water, [α — 18 2°

Hydroshikimic Acid Dibromide, $C_7H_{10}Br_2O_5$. Rho sphenoids.

Water .... $c = 14\ 263$, $t = 16°$, $[\alpha]_D = -58°$[1]

α-ISOTRIOXYSTEARIC ACID, $C_{17}H_{32}(OH)_3COOH$.

Glacial acetic acid . . $c = 10$ to 15, $[\alpha]_D = -6\ 25$ to 6.0[2]

II. Acids with Six Atoms of Oxygen

For the aldehydes, see group 16 (oxyaldehydes, sugars

ARABONIC ACID, $C_5H_{10}O_6$ Left rotating.

In solution passes gradually into the lactone. On the ch in rotation, see §75

Strontium Salt, $Sr(C_5H_9O_6)_2 + 5H_2O$. Crystals.

Water . $c = 4\ 353$ (at 100°), $t = 20°$, $[\alpha]_D = +1.96°$[3]

Anhydride, $C_5H_8O_5$. Crystals. Melting-point 89°

Water... $[\alpha]_D = -63\ 37$[4]
Water . $p = 9\ 45$, $d_4^{20} = 1.0316$, $t = 20°$, $[\alpha]_D = -73.9°$[5]

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[1] Eykman

[2] Walden Ber d chem Ges , 27, 3471.

[3] Allen and Tollens Ann Chem (Liebig), 260, 313.

[4] Bauer . J. prakt Chem , [2], 34, 47

[5] Fischer, Piloty Ber d chem Ges , 24, 4215

[6] Fischer and Piloty

RIBONIC ACID, $C_5H_{10}O_6$.

Cadmium Salt, $Cd(C_5H_9O_6)_2$ (at 100°). Fine needles

Water.............. $t = 20°$, $[\alpha]_D = +0.6°$[1]

Anhydride, $C_5H_8O_5$. Crystals. Melting-point 72° to 76°.

Water............. $c = 9.340$, $t = 20°$, $[\alpha]_D = -18.0°$[2]

The rotation remained twelve hours unchanged.

XYLONIC ACID, $C_5H_{10}O_6$. See §75.

Strontium Salt, $Sr(C_5H_9O_6)_2 + 6H_2O$. Crystals

Water.... $c = 4.305$, (at 100°), $t = 20°$, $[\alpha]_D = +12.14°$[3]

The rotation remained constant.

LYXONIC ACID LACTONE, $C_5H_8O_5$

Water . $p = 9.783$, $d = 1.035$, $t = 20°$, $[\alpha]_D = +82.4°$[4]

GLUCOSACCHARINIC ACID ANHYDRIDE, SACCHARIN, $C_6H_{10}O_5$. Made from dextrose by heating with lime.[5] Rhombic prisms. Melting-point 160° to 161°.

Water .... $[\alpha]_D = +93.1°$[6]
Water... $p = 12.077$, $d^{17.5} = 1.0365$, $t = 17.5°$, $[\alpha]_D = +93.8°$[7]
Water .. $c = 4.257$ (100°), $t = 20°$, $[\alpha]_D + 93.05°$ } [8]
" 3.688 " , " , $+93.12$ }

On standing, the rotation is decreased because of change into the acid. See §75 The rotation diminishes also on elevation of temperature.[9]

The salts rotate to the left. Scheibler gives for the sodium salt $[\alpha]_D = -17.2°$, and for the calcium salt $[\alpha]_D = -5.7°$.

MALTOSACCHARINIC ACID ANHYDRIDE, ISOSACCHARIN, $C_6H_{10}O_5$ Monoclinic crystals. Melting-point 95°.

Water $p = 9.471$ (air dry), $d_4^{20} = 1.0302$, $t = 20°$, $[\alpha]_D = +61.88°$[10]
Water $c = 10$ (air dry), $t = 10°$, $[\alpha]_D = +62.97°$[11]

Shows no multirotation

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[1] Fischer and Piloty

[2] Fischer and Piloty *Loc cit*

[3] Allen and Tollens *Loc cit*

[4] Fischer, Bromberg Ber d chem Ges, **29**, 583

[5] Kiliani *Ibid*, **15**, 2954

[6] Peligot Compt rend, **90**, 1141

[7] Scheibler Ber d chem Ges, **13**, 2216

[8] Herrmann, Tollens *Ibid*, **18**, 1333

[9] Schnelle and Tollens, Ann. Chem (Liebig), **271**, 66

[10] Wehmer, Tollens *Ibid*, **243**, 323

[11] Schnelle and Tollens

METASACCHARINIC ACID ANHYDRIDE, METASACCHARI $C_6H_{10}O_5$. Rhombic crystals. Melting-point 141 to 142°.

Water.... $p = 7.846$, $d = 1.026$, $t = 14°$, $[\alpha]_D = -48.4°$ [1]
" .... $c = 10$, $t = 20°$, $[\alpha]_D = -46.7°$
" .... 7.0, " $-46.96°$ [2]

Shows no multirotation.

The parasaccharinic acid of Kiliani[3] is left rotating.

RHAMNONIC ACID (Isodulcitonic acid), $C_6H_{12}O_6$. See §7.

ISORHAMNONIC ACID LACTONE, $C_6H_{10}O_5$. Melting-poi 150° to 152°

Water........ $p = 8.903$, $d = 1.032$, $[\alpha]^{20}_{D} = -62.02°$ [4]

After twenty-four hours by change into the acid, $[\alpha] = -5.21$

DIGITALONIC ACID, $C_{17}H_{14}O_8$. From the mixture of sugar which result from the resolution of pure digitalin.

Anhydride, rhombic crystals. Melting-point 138° to 139°.

Water..... $p = 3.3327$, $d = 1.0084$, $t = 28°$, $[\alpha]_D = -79.4°$ [5]

Tartaric Acids, $CO_2H.CHOH.CHOH.CO_2H$.

d-TARTARIC ACID.—The following formulas have been given to show the relation of the specific rotation in aqueous solution to the concentration c or to the percentage strength p of acid, or finally to the percentage amount of water q in the solutions

1 Arndtsen.[6] Determined by the Broch method for different Fraunhofer lines.

$$\left.\begin{aligned}
[\alpha]_C &= +2.748 + 0.09446\,q \\
[\alpha]_D &= +1.950 + 0.13030\,q \\
[\alpha]_E &= +0.153 + 0.17514\,q \\
[\alpha]_b &= -0.832 + 0.19147\,q \\
[\alpha]_F &= -3.598 + 0.23977\,q \\
[\alpha]_e &= -9.657 + 0.31437\,q
\end{aligned}\right\}\begin{array}{c}\text{for } q = 50 \text{ to } 95, \\ \text{and } t = 24°.\end{array}$$

The formula for $[\alpha]_D$ according to Sonnenthal[7] obtains even for a 0.2 per cent. solution.

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[1] Kiliani · Ber d chem Ges, **16**, 2627

[2] Schnelle and Tollens

[3] Ber d chem Ges, **26**, 1649

[4] Fischer, Herborn *Ibid*, **29**, 1964

[5] Kiliani *Ibid*, **25**, 2116

[6] Ann chim phys, [3], **54**, 403; Pogg. Ann, **105**, 312

[7] Wiener Akad, **100**, Abth II b, 573

2. Hesse.[1]

$$\begin{array}{llll} [\alpha]_D = 14.90 - 0.14c \text{ holds for } & c = 5 \text{ to } 15, & t = 15^\circ \\ 15.11 - 0.14c \quad `` \quad `` & 5 \text{ `` } 15, & \phantom{t = }20 \\ \phantom{[\alpha]_D = }15.22 - 0.14c \quad `` \quad `` & \phantom{c = }5 \text{ `` } 15, & 22.5, \end{array}$$

in which the middle formula was calculated from the other two.

3. Landolt.[2]

$$[\alpha]_D = 15.06 - 0.131c, \quad c = 0.5 \text{ to } 15, \quad t = 20^\circ$$

4. Pribram.[3]

$$[\alpha]_D = 14.770 - 0.1321p, \quad p = 1 \text{ to } 5, \quad t = 20^\circ$$

5. Th Thomsen[4]

$$\begin{array}{rll} [\alpha]_D = + 14.154 - 0.1644p & p = 20 \text{ to } 50 & \multirow{2}{*}{$\Big\} \; t = 10^\circ$} \\ - 2.286 + 0.1644q & q = 50 \text{ to } 80 & \\ + 14.615 - 0.1588p & p = 20 \text{ to } 50 & \Big\} \; t = 15^\circ \\ - 1.265 + 0.1588q & q = 50 \text{ to } 80 & \\ + 15.050 - 0.1535p & p = 20 \text{ to } 50 & \Big\} \; t = 20^\circ \\ - 0.300 + 0.1535q & q = 50 \text{ to } 80 & \\ + 15.429 - 0.1480p & p = 20 \text{ to } 50 & \Big\} \; t = 25^\circ \\ + 0.629 + 0.1480q & q = 50 \text{ to } 80 & \\ + 15.784 - 0.1429p & p = 20 \text{ to } 50 & \Big\} \; t = 30^\circ \\ + 1.494 + 0.1429q & q = 50 \text{ to } 80 & \end{array}$$

From these constants we have the general formula

$$[\alpha]^t_D = (13.096 + 0.1139t - 0.00081t^2) - (0.1756 - 0.001135t)p$$

With reference to the concentration c we have

$$[\alpha]_D = 13.436 - 0.1187c, \text{ for } c = 22 \text{ to } 63 \text{ and } t = 20^\circ$$

The value of the specific rotation of tartaric acid at a number of different temperatures and percentage strengths according to the Thomsen formula, is shown in the following table.

	$t =$	10°	15°	20°	25°	30°
p 50,	$[\alpha]_D =$	+5.93	+6.69	+7.38	+8.08	+8.64°
40		7.58	8.28	8.91	9.55	10.07
30		9.22	9.86	10.45	11.02	11.50
20		10.87	11.45	11.98	12.49	12.93

On the variation of the specific rotation of aqueous solutions of tartaric acid with the temperature, see §60.

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[1] Ann Chem (Liebig), 176, 120

[2] Ber d chem Ges., 6, 1073.

[3] Math naturw Abh. d. Berl. Akad., 1887, p 248

[4] J prakt Chem., [2], 32, 213

Salts of Dextrotartaric Acid

On the rotation of tartrates in dilute solutions, see §61

Potassium Acid Tartrate, $KC_4H_5O_6$.

$c = 0.615, \quad t = 20°, \quad [\alpha]_D = 22\ 61°$ [1]

In the following observations by Sonnenthal,[2] T is the between the preparation of the solution and the observatic

p	d_4^{20}.	T.	$[\alpha]_D^{20}$.
0 4116	1.0044	At once and after 48 hours	22 119°
0 3001	1 0041	At once	20 192
0 2407	1.0011	At once	22 241
"	"	48 hours	22.379
"	"	80 hours	23 025
"	"	120 hours	23.025

Sodium Acid Tartrate, $NaC_4H_5O_6 + H_2O$

1. According to Thomsen[3] the specific rotation decreas with decreasing concentration, but increases slightly with tl temperature.

Hydrate		$[\alpha]_D^{15°}$	$[\alpha]_D^{20°}$.	$[\alpha]_D^{25°}$	$[\alpha]_D^{30°}$.
p	c				
12.70	13 50	....	. .	....	22 47°
10.16	10 65	...	....	22.12	22 19
8 89	9 26	....	21.84	21.85	22 07
7 62	7.89	21.85	21.88	22 10	22 29
6.35	6 54	21 56	21 84	21.77	21.88

2. $c = 4.409, \ [\alpha]_D^{20} = 23.95°$ anhydrous (21 67 hydrate).[4]

Lithium Acid Tartrate, $LiC_4H_5O_6 + H_2O$.

Anhydrous . ..... $c = 7\ 998, \ [\alpha]_D^{20} = 27.43$[4]

Ammonium Acid Tartrate, $NH_4C_4H_5O_6$

Anhydrous .... $c = 1.712, \ [\alpha]_D^{20} = 25.65°$[4]

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[1] Landolt

[2] Wien Akad, 100, II, 510

[3] Thomsen J prakt Chem, [2], 34, 85

[4] Landolt

Thallium Acid Tartrate, $TlHC_4H_4O_6$

$$c = 1, \quad [\alpha]_D^{20} = 12.02°$$ [1]

Potassium Tartrate, $K_2C_4H_4O_6 + \frac{1}{2} H_2O$.

1. Krecke[2] found for the hydrated salt, $c = 20$ and $t = 25°$ for different rays ·

$$[\alpha]_C = 22.04, \ [\alpha]_D = 26.84, \ [\alpha]_E = 32.95, \ [\alpha]_b = 34.96, \ [\alpha]_F = 39.92°$$

The influence of temperature is slight

2. Anhydrous $c = 11.597$, $[\alpha]_D^{20} = 28.48°$ (hydrated 27.39).[3]

3. Experiments by Schütt[4] gave :

Hydrated salt		Anhydrous salt	
$c = 40$	$[\alpha]_D^{20} = 28.46°$	$c = 38.47$	$[\alpha]_D^{20} = 29.59°$
30	28.08	28.85	29.20
22	27.76	21.16	28.87
20	27.51	19.23	28.61
10	26.94	9.62	28.01

This formula follows for the anhydrous salt .

$$[\alpha]_D^{20} = 27.14 + 0.0992\,c - 0.000938\,c^2$$

On the effect of addition of KCl and NaCl on the rotation of potassium tartrate, §70, p. 245.

4. Th Thomsen[5] found these values referred to the anhydrous salt

p	c.	$[\alpha]_D^{15}$.	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$.
54.54	79.24	30.70°	30.67°	30.57°
36.39	46.55	30.07	30.06	30.01
18.09	20.38	29.02	29.19	29.26
9.07	9.62	28.34	28.49	28.65

From these observations we have the following interpolation formulas :

$$[\alpha]_D^{15} = 27.56 + 0.0925\,p - 0.00065\,p^2$$
$$[\alpha]_D^{20} = 27.62 + 0.1064\,p - 0.00108\,p^2$$
$$[\alpha]_D^{25} = 27.86 + 0.0951\,p - 0.00099\,p^2$$

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[1] Long · Am. J Sci , [3], 38, 267

[2] Arch. Néerl., VII, 1872

[3] Landolt.

[4] Ber d. chem. Ges , 21, 2586.

[5] J. prakt. Chem., [2], 34, 89.

Sodium Tartrate, $Na_2C_4H_4O_6 + 2H_2O$.

1. Hydrated $c = 5$ to 15, $t = 22.5°$, $[\alpha]_D = 27.85 -$

$[\alpha]_C$ $[\alpha]_D$ $[\alpha]_E$ $[\alpha]_b$

2. Hydrated $c = 20$, $t = 25°$. 20.82 25.79 31.67 32.7
3. Anhydrous $c = 9.946$, $[\alpha]_D^{20} = 30.85$ (hydrated = 2
4. Th. Thomsen[4] investigated the following solutions

HYDRATED SALT.

p	c	$[\alpha]_D^{15}$.	$[\alpha]_D^{20}$.	$[\alpha]_D^{25}$.	$[\alpha]_D^{30}$.
36.77	45.51	24.25	24.28	24.38	....
32.25	38.90	....	24.66	....	....
22.69	25.87	..	25.34	...	....
18.40	20.46	25.54	25.63	25.76	25.90
13.60	14.69	....	25.82	....	....
9.20	9.69	26.01	26.06	26.28	26.22
3.07	3.11	26.19	26.35	26.31	...

From this we have for $Na_2C_4H_4O_6 + 2H_2O$ the interpol formulas

$$[\alpha]_D^{15} = 26.41 - 0.03615\,p - 0.000617\,p^2$$
$$[\alpha]_D^{20} = 26.30 - 0.02020\,p - 0.000963\,p^2$$
$$[\alpha]_D^{25} = 26.65 - 0.03686\,p - 0.000693\,p^2$$

Potassium Sodium Tartrate, $KNaC_4H_4O_6 + 4H_2O$ (Roch salt).

1. Th. Thomsen[5] has experimented with solutions made saturating sodium acid tartrate with 1 mol. KOH and addi of $^1/_{100}$ mol. NaOH:

$KNaC_4H_4O_6$		$[\alpha]_D^{15}$.	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$.
p	c			
33.68	42.35	29.31	29.33	29.41
25.27	29.99	29.46	29.51	29.55
16.84	18.86	29.59	29.77	29.80
8.41	8.89	29.47	29.52	29.46

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[1] Hesse. Ann Chem (Liebig), 176, 122
[2] Krecke: Arch Néerl, VII, 1872
[3] Landolt.
[4] J prakt Chem, [2] 34, 79
[5] *Ibid*, [2], 34, 90

From this, calculated by Schütt, $[\alpha]^{20}_D = 29.73 - 0.0078\,c$ for $c = 8$ to 43.

2. J H. Long.[1]

$c =$	5	15	25	35	45
$[\alpha]^{20}_D$ hydrated……	22 14	22.16	22.12	22.13	22.06
$[\alpha]^{20}_D$ anhydrous ….	29.73	29 76	29 70	29.72	29 62

From this, calculated by Schütt, $[\alpha]^{20}_D =$ 29 77 $- 0.0026\,c$ (anhydrous) for $c = 5$ to 45.

3. Krecke[2] determined the specific rotation of a solution with $c = 20$ for different rays ; $t = 25°$.

		$[\alpha]_C$	$[\alpha]_D$	$[\alpha]_E$	$[\alpha]_b$	$[\alpha]_F$
Hydrated	$c = 20$	18 52	22 42	26 49	27 67	32 08

4. Anhydrous $c = 10.77$, $[\alpha]^{20}_D = 29.67°$.[3]

Lithium Tartrate, $Li_2C_4H_4O_6$.

Anhydrous $c =$ 8 305, $[\alpha]^{20}_D =$ 35 84°.[3]

Ammonium Tartrate, $(NH_4)_2C_4H_4O_6$

1. $c =$ 9 433, $[\alpha]^{20}_D =$ 34 26.[3]

2 Krecke[4] found for different rays

Anhydrous ……	$[\alpha]^{25}_C$	$[\alpha]^{25}_D$	$[\alpha]^{25}_E$	$[\alpha]^{25}_b$	$[\alpha]^{25}_F$
$c = 20$ ………	31 08	37.09	43 05	45 27	53 76

Potassium Ammonium Tartrate, $KNH_4C_4H_4O_6$.

$c =$ 10 515, $[\alpha]^{20}_D = +$ 31 11[3]

Addition of NH_4Cl and of NaCl decreases the rotation, while that of KCl increases it, but apparently irregularly and not in proportion to the amount of salt added.[5]

$c = 20$, $[\alpha]^{20}_D =$ 30 85°

In 100 cc along with 20 grams of tartrate	$[\alpha]^{20}_D$	Δ
5 grams NH_4Cl …….	30 66	— 0 19
10 " " ……….	30 60	— 0 25
5 grams KCl…………	30 89	+ 0 04
10 " " ……….	31 42	+ 0 57
5 grams NaCl…………	29 96	— 0 89
10 " " ……………	28 51	— 2 34

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[1] Am J Sci, 36, 353
[2] Arch. Néerl, VII
[3] Landolt
[4] Arch Néerl., VII.
[5] Long: Am J. Sci, [3], 40, 282.

Sodium Ammonium Tartrate, $NaNH_4C_4H_4O_6 + 4H_2O$. Rhombic columns.

$c = 9\ 690$ (anhydrous), $[\alpha]_D^{20} = 32.65°$ [1]

Magnesium Tartrate, $MgC_4H_4O_6$

$c = 8.818$, $[\alpha]_D^{20} = 35\ 86°$ [1]

Borohydrotartrate, Boryltartrate, Borotartaric Acid, $BO.H.C_4H_4O_6$ See §70

Potassium Borotartrate, $KBOC_4H_4O_6$.

Obtained in aqueous solution by addition of 1 mol. of boric acid to 1 mol. of potassium acid tartrate

$$1.\quad \left.\begin{array}{ll} c = 2.744, & [\alpha]_D^{20} = 51.48 \\ c = 5.488, & [\alpha]_D^{20} = 58.35 \end{array}\right\}^{1}$$

$$2.\quad \left.\begin{array}{llll} c = \ \ 5 \text{ (dried at } 100°) & t = 20°, & [\alpha]_D & = 58.10° \\ c = 20 \text{ (`` `` `` )} & \text{``} & \text{``} & = 68\ 29 \\ c = 10 \text{ (dried over } H_2SO_4) & \text{``} & \text{``} & = 59.06 \\ c = 10 \text{ ( `` `` ``)} & t = 29 & \text{``} & = 57.29 \end{array}\right\}^{2}$$

From the observations of Long there follows according to Schütt:

$$[\alpha]_D = 50\ 67 + 1\ 688\ c - 0.04036\ c^2, \text{ for } c = 5 \text{ to } 20$$

Addition of alkali salts (especially potassium acetate) increases the specific rotation.[3]

Sodium Borotartrate, $NaBOC_4H_4O_6$

From equal molecules of H_3BO_3 and $NaHC_4H_4O_6$ in aqueous solution:

$$\left.\begin{array}{ll} c = \ \ 2\ 538, & [\alpha]_D^{20} = 55\ 02° \\ c = \ \ 5\ 075, & \quad \text{``} \ \ = 63.48 \\ c = 10\ 151, & \quad \text{``} \ \ = 71.47 \end{array}\right\}^{1}$$

Arsenyl Tartaric Acid, $AsOC_4H_5O_6$.

Made in solution by heating two molecules of tartaric acid with one molecule of arsenous oxide.

$c = 12.304$, $[\alpha]_D^{20} = 16\ 91°$ [1]

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[1] Landolt

[2] Long Am J. Sci., 38, 264

[3] Long. *Ibid*, [3], 38, 271

Potassium Arsenyl Tartrate, $KAsOC_4H_4O_6$.

Made by heating two molecules of cream of tartar with one molecule of arsenous oxide to complete solution.

$$c = 0.563, \quad [\alpha]_D^{20} = 21\ 13°\ ^1$$

Sodium Arsenyl Tartrate, $NaAsOC_4H_4O_6$.

Made in solution from As_2O_3 and $NaHC_4H_4O_6$.

$$c = 3\ 358, \quad [\alpha]_D^{20} = 20.64°\ ^1$$

Potassium Antimonyl Tartrate, *Tartar Emetic*, $2(KSbOC_4H_4O_6) + H_2O$.

1. $c = 5$, $t = 25°$	$[\alpha]_C$	$[\alpha]_D$	$[\alpha]_E$	$[\alpha]_b$	$[\alpha]_F$
Hydrated salt	111.82	138 66	180.39	187 39	218.74°.[2]

2. Anhydrous $c = 5$, $t = 20°$, $[\alpha]_D = + 141.27°$.[3]

3. Anhydrous $c = 7.982$, $[\alpha]_D^{20} = 142.76°$, from which
Hydrated $[\alpha]_D^{20} = 138.89$.[1]

On the effect of addition of alkali salts on the rotation of tartar emetic, see experiments by Long.[4]

Thallium Tartrate, $2Tl_2C_4H_4O_6 + H_2O$.

$$c = 5 \quad \cdot\ \cdot\ [\alpha]_D^{19} = 4.582°, \quad [\alpha]_D^{20} = 4\ 758°, \quad [\alpha]_D^{28\ 4} = 5\ 704°$$

The specific rotation increases with rising temperature and also by addition of potassium and sodium salts, especially by potassium carbonate.[5]

Thallium Potassium Tartrate, $TlKC_4H_4O_6$

$$\begin{array}{lll} c = 5 & t = 20° & \left.\begin{array}{l}[\alpha]_D = 10\ 057° \\ \quad \text{''} = 8\ 840 \\ \quad \text{''} = 8\ 173\end{array}\right\}^6 \\ c = 10 & t = 20 & \\ c = 20 & t = 20 & \\ c = 10 & t = 30 & \quad \text{''} = 10.092\ ^7 \end{array}$$

Potassium and sodium salts increase, but thallium salts diminish, the rotation.

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[1] Landolt.

[2] Krecke · Arch Néerl , VII

[3] Long : Sill. Am J Sci , [3], **38**, 264.

[4] *Ibid.*, [3]. **38**, 264 ; **40**, 275 See §70, p. 245

[5] Long : Am J. of Sci , [3] **38**, 266.

[6] From this according to Schutt . $[\alpha]_D^{20} = 11\ 672 - 0.3788c + 0\ 01025c^2$, c — 5 to 20

[7] Long . *Loc cit.*

Thallium Sodium Tartrate, $TlNaC_4H_4O_6 + 4H_2O$.

$c = 5$ (hydrated) $t = 20$ $[\alpha]_D = 9.07°$
$c = 20$ " $t = 20$ " $= 6.49$
$c = 10$ (anhydrous) $t = 20$ " $= 8.60$
$c = 10$ " $t = 28$ " $= 9.49$[1]

Sodium sulphate increases and thallium sulphate diminishes the specific rotation.

Thallium Ammonium Tartrate, $TlNH_4C_4H_4O_6$.

$c = 5$ $[\alpha]_D^{20} = 10.03°$
$c = 20$ $[\alpha]_D^{20} = 7.56$ [1]

Increase of temperature and addition of potassium salts increase the specific rotation.

Thallium Lithium Tartrate, $TlLiC_4H_4O_6 + H_2O$.

$c = 5$ (hydrated) $[\alpha]_D^{20} = 9.46°$
$c = 20$ " " $= 6.69$ [1]

Lithium salts increase and thallium sulphate diminishes the specific rotation.

Thallium Antimonyl Tartrate, $TlSbOC_4H_4O_6 + H_2O$.

$c = 2$ $t = 20°$ $[\alpha]_D = 100.44°$
$c = 2$ $t = 28$ " $= 99.64$ [1]

Acetates produce a decrease in the specific rotation.

Ethylene Diamine Ditartrate, $C_2H_8N_2.2C_4H_6O_6$

Water .... $c = 1.44$ $[\alpha]_D^{18} = 170.03°$
Water .... $c = 0.36$ " $= 170.83$ [2]

On the rotation of certain tartrates in glycerol solution, see experiments by Long.[3]

d-Tartaric Acid Esters

Monomethyl Tartrate (*Methyl Tartaric Acid*), $HCH_3C_4H_4O_6$. Sirup.

Water. .... $c = 2.073$ $[\alpha]_D = 18.1°$
Alcohol .... $c = 1.037$ " $= 3.22$

The salts of methyl tartaric acid are crystalline

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[1] Long, *Loc cit*
[2] Colson Compt rend, **115**, 729
[3] J Am Chem Soc, **23**, 813

		c Anhydrous	$[\alpha]_D$		c	l	α_D.[1]
Li salt......	Water	2.148	26 5°	Alcohol	0.1612	6 dm	0.14°
NH_4 "	"	2.291	28.0	"	....	..	....
K "	"	2.557	22.7	"	0.0088	6 dm.	0 02
Na "	"	2.353	21 0	"	0.0260	6 dm.	0.04

Monoethyl Tartrate (*Ethyl Tartaric Acid*), $HC_2H_5C_4H_4O_6$. Sirup.

Water............... $c = 2.252$ $[\alpha]_D = 21\ 8°$
Alcohol .... $c = 1\ 126$ " $= 7\ 10$

Ethyl Tartaric Acid Salts. Crystalline [1]

		c Anhydrous	$[\alpha]_D$		c	l	α_D
Li salt. .	Water	2 329	28 8°	Alcohol	0.7052	6 dm	0 87°
Na "	"	2 531	27 5	"	0 0892	6 dm	0.10
K "	"	2 730	21 6	"	0 0308	6 dm	0 04
Ca "	"	2 490	24 3	...	.	...	..
Ba "	"	3 107	20 3	. .	...	....	...

Dimethyl Tartrate, $(CH_3)_2C_4H_4O_6$. Crystals Melting-point 48°; boiling-point 158.5° (12 mm.), 280° (760 mm.).[2]

Liquid, $d^{15} = 1\ 3403$ $[\alpha]_D^{18} = 1\ 83°$ [3]
$d^{20} = 1\ 3284$ $[\alpha]_D^{20} = 2.14°$ [4]
$d^{100} = 1\ 2500$ $[\alpha]_D^{10} = -6\ 00$

Diethyl Tartrate, $(C_2H_5)_2C_4H_4O_6$ Liquid, boiling-point 280° (760 mm.).

$d^{14} = 1.2097$ $[\alpha]_D^{18} = 7\ 47°$ [5]
$d^{20} = 1\ 2059$ $[\alpha]_D^{20} = 7\ 66$
$d^{100} = 1.1279$ $[\alpha]_D^{100} = 13\ 29$ [6]

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[1] Fayollat. Compt rend, 117, 630.
[2] Anschutz · Ber d chem, Ges., 18, 1399
[3] Anschütz, Pictet *Ibid*, 13, 1117, 1538
[4] Pictet Arch. sc phys nat. [3], 7, 82; Jahresbericht, 1882, p. 856
[5] Anschütz Pictet · *Loc cit.*
[6] Pictet : Jsb. Chem., 1882, p. 856.

Di-n-propyl Tartrate, $(C_3H_7)_2C_4H_4O_6$. Liquid, boiling-point 303° (760 mm.).

$$d^{17} = 1.1392 \quad [\alpha]_D^{18} = 12\ 09°\ ^{1}$$
$$d^{20} = 1.1344 \quad [\alpha]_D^{20} = 12\ 44$$
$$d^{100} = 1\ 0590 \quad [\alpha]_D^{100} = 17\ 11\ ^{2}$$

Diisopropyl Tartrate, $(CH_3.CH_3\ CH)_2C_4H_4O_6$. Liquid, boiling-point 275° (760 mm)

$$d^{20} = 1\ 1300 \quad [\alpha]_D^{20} = 14\ 89°$$
$$d^{100} = 1\ 0537 \quad [\alpha]_D^{100} = 18\ 82\ ^{2}$$

Diisobutyl Tartrate, $[(CH_3)_2CH.CH_2]_2C_4H_4O_6$. Solid, melting-point 68°, boiling-point 323° to 325° (760 mm.).

$$d^{100} = 1\ 0145 \quad [\alpha]_D^{100} = 19\ 87°\ ^{2}$$

Potassium Ethyl Tartrate, $KC_2H_5C_4H_4O_6$

Water.. . $c = 11.079$ $[\alpha]_D^{20} = 29\ 91°$[3]

Barium Ethyl Tartrate, $Ba(C_2H_5.C_4H_4O_6)_2$.

Water. .. $c = 12.586$ $[\alpha]_D^{20} = 25.68°$[3]

d-Diacetyl Tartaric Acid Compounds

d-Diacetyl Tartaric Acid,

$$COOH.CH(OC_2H_3O).CH(OC_2H_3O).COOH.$$

(Also with $3H_2O$.) Left rotating in water, methyl alcohol and ethyl alcohol (Pictet), also in ether and benzene.[4]

Water $c =$ 17.947 14.357 11.486 9 189 7.351 4.705 3 764
" $[\alpha]_D^{22} = -23.04\ -22.48\ -22\ 16 - 21.50\ -21\ 33\ -20\ 07\ -\ 19.32°$
Alcohol .... $c =$ 7.367 4 911 3 274
" .... $[\alpha]_D^{22} = -23\ 63$ -23.14 $-21.52°$
Methyl alcohol ($d = 0\ 824$).. $c = 4.681$ $[\alpha]_D^{15} = -23\ 74°$[5]

The sodium and barium salts are also left rotating[6]

d Diacetyl Tartaric Acid Anhydride, $(C_2H_3O.O)CH.CO)_2O$. Right rotating. Prismatic crystals. Melting-point 125° to 129°.

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[1] Anschutz, Pictet . *Loc. cit*
[2] Pictet . *Loc cit*
[3] Landolt
[4] Colson Compt rend , 114, 175
[5] Pictet Jsb Chem , 1882, p 856, 857.
[6] Anschutz, Pictet Ber d chem Ges., 13, 1178

	In benzene		In acetone	
$c =$	2 091	1 045	11 656	4 403
$[\alpha]_D =$	$+$ 58 69	$+$ 63 05°	$+$ 59 70	$+$ 62 04° [1]

The esters of diacetyl tartaric acid may be distilled at the ordinary temperature without suffering a change in their rotating power [2]

Dimethyl Ester, $(CH_3)_2(C_2H_3O)_2C_4H_2O_6$. Rhomboidal prisms. Melting-point 103°. According to Pictet[3] left rotating.

Alcohol ($d = 0$ 826) .... $c = 3$ 566 $[\alpha]_D^{18} = -$ 14 23° [1]

" " .. .... $c = 3$ 254 $[\alpha]_D^{15} = -$ 14 29

Diethyl Ester, $(C_2H_5)_2(C_2H_3O)_2C_4H_2O_6$. Triclinic prisms. Melting-point 66.5°, boiling-point 291° to 292°. $[\alpha]_D$ for the uperfused ester $= +$ 5 0°.[4]

Alcohol ($d = 0$ 826) .. .. $c = 23$ 644 $[\alpha]_D^{17} = +$ 1 02° [1]

On the rotation in chloroform solution see §57.

N-Dipropyl Ester, $(C_3H_7)_2(C_2H_3O)_2.C_4H_2O_6$ Crystals, melt-ng-point 31°, boiling-point 313°.

Alcohol ($d = 0$ 826)...... $c = 7$ 855 $[\alpha]_D^{14} = +$ 7 04° [1]

" " ... . $c = 3$ 253 $[\alpha]_D^{15} = +$ 6 52

According to Freundler,[5] the ester is liquid at the ordinary emperature, $[\alpha]_D = 13.5°$ Its specific rotation changes greatly with solution in different liquids See §59.

N-Dibutyl Ester, $(C_4H_9)_2(C_2H_3O)_2C_4H_2O_6$ Liquid. $t = 20°$, $[\alpha]_D = +$ 17.8°.[4]

Diisobutyl Ester, $(C_4H_9)_2(C_2H_3O)_2$ $C_4H_2O_6$ Liquid Boiling-point 322 to 326° $t =$ about 20°, $[\alpha]_D = +$ 11.3° [4]

Alcohol ($d = 0$ 826).. $c = 13$ 559 $[\alpha]_D^{14} = +$10 51° [1]

" " $c =$ 7 953 $[\alpha]_D^{15} = +$ 10 29

Compounds of *diacetyl tartaric acid* with ethylene diamine.

Neutral Salt, $C_2H_8N_2$ $2C_8H_{10}O_8$ Crystals.

Water .... $c = 11$ 5 $[\alpha]_D = -$ 12 74°

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[1] Pictet

[2] Freundler, Compt rend, **115**, 509

[3] *Loc cit*

[4] Freundler

[5] Compt rend, **117**, 556

Acid Salt, $C_2H_8N_2.C_8H_{10}O_8$. Crystals.

Water..........	$c = 11.5$	$[\alpha]_D = -17.05°$ [1]

Numerous further determinations of rotation of ester dipropionyl, dibutyryl, di-*n*-valeryl and di-*n*-caproyl tart acid have been made by Freundler.[2]

For the rotation of the esters of di-monochloracetyl tart acid, see Franklin and Turnbull.[3]

See McCrae and Patterson[4] for other derivatives of diace tartaric acid

Compounds of d-Dibenzoyl Tartaric Acid.

Dibenzoyl Tartaric Acid, $COOH.CH.O(C_7H_5O)CH.O(C_7H_5O).COOH + H_2O$. Crystals Melting-point 9

With Water of Crystallization :

Alcohol ($d = 0.818$).........	$c = 8.933$	$[\alpha]^{17}_D = -110.91°$
" "	$c = 4.994$	$[\alpha]^{15}_D = -112.05$
Methyl alcohol	$c = 4.857$	$[\alpha]^{19}_D = -116.30$

Anhydrous

Alcohol ($d = 0.818$)...... ..	$c = 8.506$	$[\alpha]^{17}_D = -116.47°$ [5]
" "	$c = 4.755$	$[\alpha]^{15}_D = -117.68$
Methyl alcohol	$c = 4.625$	$[\alpha]^{19}_D = -122.14$

Dibenzoyl Tartaric Acid Anhydride, $(C_7H_5O.O.CH\ CO)_2$(Crystals. Melting-point 174°.

Acetone.	$c = 4.644$	$[\alpha]^{18}_D = +142.94°$
"	$c = 1.572$	$[\alpha]^{18}_D = +143.22$ [6]
		$[\alpha]_D = +114$ [7]

Dibenzoyl Tartaric Acid Dimethyl Ester, $(CH_3)_2(C_7H_5O)C_4H_2O_6$. Crystals. Melting-point 132°.

Alcohol..	$c = 0.245$	$[\alpha]^{20}_D = -96.61°$
Chloroform	$c = 11.612$	$[\alpha]^{19}_D = -88.24$
"	$c = 8.598$	$[\alpha]^{19}_D = -88.78$ [6]

Dibenzoyl Tartaric Acid Diethyl Ester, $(C_2H_5)_2(C_7H_5O)C_4H_2O_6$. Liquid.

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[1] Colson Compt rend, **115**, 729

[2] Compt. rend, **115**, 509, 556; Bull soc chim, [3], **9**, 680, **11**, 366, 470, **13**, 1055 Ann Chim. Phys, [7], **3**, 433, **4**, 244

[3] J. Chem Soc, **73**, 203 (1899)

[4] *Ibid*, **77**, 1096 (1900)

[5] Pictet Jsb Chem, 1882, p 857.

[6] Pictet.

[7] Freundler Bull soc. chim, [3] **7**, 804.

Alcohol ($d = 0.815$) .. $c = 9.175$ $[\alpha]_D^{16} = -54\ 50°$
" " ... $c = 5.733$ $[\alpha]_D^{16} = -57\ 72$
" " . $c = 2.693$ $[\alpha]_D^{19} = -60.02$ [1]

Dibenzoyl Tartaric Acid Diisobutyl Ester, $(C_4H_9)_2(C_7H_5O)_2.C_4H_2O_6$. Liquid.

Alcohol ($d = 0\ 818$) $c = 14\ 085$ $[\alpha]_D^{22} = -48\ 86°$
" " $c = 4\ 922$ $[\alpha]_D^{19} = -42\ 94$
" " $c = 2\ 880$ $[\alpha]_D^{19} = -41\ 95$ [1]

Diphenyl Acetyl Tartaric Acid Anhydride, $(C_7H_7.CO_2.CH.CO)_2O$ $[\alpha]_D = +58°$.[2]

Diphenyl Propionyl Tartaric Acid Anhydride, $(C_8H_9\ CO_2.CH.CO)_2O$. $[\alpha]_D = +38°$.[3]

Frankland and Wharton[4] and Frankland and McCrae[5] have given the following determinations .

	t	$[\alpha]_D$.
Diethyl monobenzoyl tartrate....	24°	+ 20 71°
	38	+ 20 18
	63	+ 19.02
	79	+ 18 43
	99.5	+ 17 69
	135.0	+ 16 36
Dimethyl dibenzoyl tartrate..	100	— 72 56
	137	— 66 84
	183	— 58 94
Diethyl dibenzoyl tartrate.......	18	— 59 36
	38	— 61 70
	44	— 62 05
	53 5	— 62 28
	60	— 62 28
	100	— 60 77
Diethyl monoorthotoluyl tartrate	14	+ 12.08
	20	+ 11 82
	32 5	+ 11 74
	65	+ 11 20
	100	+ 10 88
	136.5	+ 10 62

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[1] Pictet

[2] Freundler Bull soc chim , [3], **7**, 804

[3] Freundler

[4] J Chem Soc., **69**, 1309, 1583 (1896)

[5] *Ibid* , **73**, 307 (1898).

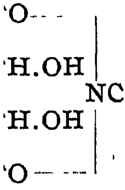
	t	[α]
Diethyl monometatoluyl tartrate	14.5	+ 13.63
	20	+ 13.59
	54	+ 13.28
	100	+ 12.57
	136	+ 11.92
Diethyl monoparatoluyl tartrate	100	+ 15.85
	109	+ 15.44
	138	+ 14.59
	180	+ 13.38
Dimethyl diorthotoluyl tartrate	12	− 77.82
	19	− 78.42
	33.5	− 77.00
	54.5	− 74.23
	70	− 72.02
	100	− 68.10
	136	− 61.28
Dimethyl dimetatoluyl tartrate	100	− 79.02
	136	− 70.58
	183	− 60.96
Dimethyl diparatoluyl tartrate	100	− 102.82
	135.5	− 91.52
	183	− 76.90
Diethyl diorthotoluyl tartrate	11	− 60.37
	30	− 60.33
	49	− 59.53
	70	− 57.96
	100	− 54.73
	135	− 50.37
Diethyl dimetatoluyl tartrate	20.5	− 69.31
	24.5	− 68.87
	44.5	− 69.16
	50	− 69.00
	100	− 63.74
	136	− 58.71
Diethyl diparatoluyl tartrate	100	− 89.98
	137	− 81.46
	183.5	− 69.50

The observations were made in tubes 44 to 50 mm. in length, and specific gravity determinations were made over a sufficiently wide range of temperature to allow the calculation of the specific rotation.

Imides of d-Tartaric Acid and Benzoyl Tartaric Acid

The following data are from Ladenburg.[1]

Methyl Tartrimide. Made by heating methylamine bitartate, by which partial racemization followed. Melting-point 78°.



$$\left.\begin{array}{l} \text{O---} \\ \text{H.OH} \\ \text{H.OH} \\ \text{O---} \end{array}\right| \text{NCH}_3$$

Water, $p = 7.31$ $d = 1.0242$ $[\alpha]_D = +194.2°$

" $p = 9.04$ $d = 1.0291$ " $= +193.6$

" $p = 12.94$ $d = 1.0445$ " $= +192.6$

From which $[\alpha]_D = 196.30 - 0.2877\,p$ for $p = 7$ to 13

By heating methyl tartrimide with 2 mols. of benzoyl chloide there result .

α-Dibenzoyl Methyl Tartrimide. Melting-point 56°

Ethyl acetate . . . . $p = 7.93$ $[\alpha]_D = +183.9°$

" " . . . . $p = 15.83$ " $= +185.7$

β-Dibenzoyl Methyl Tartrimide Melting-point 106° to 108°

Ethyl acetate . . . . $p = 7.93$ $[\alpha]_D = +188.8°$

" " . . . . $p = 15.84$ " $= +189.8$

Ethyl Tartrimide, $C_4H_4O_4\,NC_2H_5$. Melting-point 171° to 74°.

Water . . . . $p = 5.76$ $[\alpha]_D = +164.9°$

" . . . . $p = 7.32$ " $= +165.6$

" . . . . $p = 8.57$ " $= +166.2$

Changes in the Specific Rotation of d-Tartaric Acid in Presence of Inactive Substances

If different bodies are added to aqueous solutions of tartaric cid, the degree of its electrolytic dissociation, as explained in 61, is altered, and as the latter is reduced, the specific rotaion is lowered. This follows on addition of acids, alkalies, lcohols and other bodies and the decrease in the right rotation, o caused, may extend in certain cases to inactivity, or even to a hange to left rotation. When an increase in activity is oberved, as by addition of boric acid, molybdic acid, or alkalies, his depends on the formation of complex compounds of tararic acid, as referred to also in §61.

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[1] Ber. d chem Ges, **29**, 2710

Of the many observations bearing on this, a number have been referred to in the general part of the work (see §§59, 61, 70); in regard to others, it is sufficient here to refer to the original papers. Most of these have a limited value only, because they are based on determinations with but few concentrations, and the corresponding data concerning the degree of dissociation are lacking.

Inorganic and Organic Acids (see §61). These produce a decrease in the right rotation.[1] Amido-acetic acid and amido-propionic acid increase the activity.

Alkalies bring about a decrease in the right rotation of alkali tartrates, which may extend to left rotation.[2]

Alkali Salts produce sometimes an increase, sometimes a decrease in the rotation of the tartrates. §70.[3]

Molybdates and Tungstates. Increase in rotation to a maximum point. §70.

Alcohols. Decrease in rotation.[4]

Acetone. Decrease.[5]

Benzene and Homologues, mixed with alcohol, produce left rotation. §59.[6]

Organic Haloid and Nitro Compounds Decrease in the right rotation or change to left rotation. §59.[7]

Inactive Organic Bases (aniline, pyridine). The right rotation increases to a maximum and then decreases.[8]

Amido compounds (urea, glycocoll, alanin) produce increase in the rotation. Urea,[9] glycocoll, alanin.[10]

l-TARTARIC ACID. 1. Water $p = 35.7$, $t = 17°$; Biot's red ray $[\alpha]_r = -8.43°$.

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[1] Biot · Mem de l'Acad., **16**, 229. Landolt · Ber. d chem. Ges., **13**, 2331. Th. Thomsen. J. prakt Chem., [2], **32**, 219; Pribram. Sitzber. Wien. Akad., **97**, II, 13.

[2] Th Thomsen J prakt. Chem., [2], **35**, 145 Aignan. Compt. rend., **112**, 1000

[3] F Schütt. Ber. d chem. Ges., **21**, 2586 (KCl and NaCl). Long · Sill. Am. J. Sci., [3], **36**, 351, **38**, 264, **40**, 275 Th Thomsen: J. prakt. Chem., [2], **34**, 83.

[4] Biot · Mem de l'Acad, **15**, 240. Landolt · Ber. d. chem. Ges., **13**, 2332. Pribram · Sitzber. Wien. Akad. **97**, II, 468.

[5] Landolt: Ber d. chem. Ges., **13**, 2332. Pribram: Sitzber Wien. Akad., **97**, II, 463.

[6] Pribram: Ber. d chem. Ges., **22**, 6

[7] Pribram: *Ibid.*, **22**, 7.

[8] Pribram *Ibid.*, **22**, 9.

[9] Pribram: *Ibid.*, **22**, 8.

[10] Pribram Sitzber Wien Akad., **97**, II, 479.

For right tartaric acid under the same conditions, $[\alpha]_r = + 8.58$

2. The review of Pasteur's[1] observations by a committee consisting of Biot, Dumas, Regnault, and Balard furnished the following values:[2]

	p	d^{27}_4.	l.	t	α_r.	$[\alpha]_r$.
Levotartaric acid..	42.06	1.21785	5.198	20.5°	$-21.485°$	$-8.070°$
Dextrotartaric acid	41.97	1.21765	5.198	20.5	$+21.452$	$+8.082$

Addition of boric acid increases the left rotation in the same degree that it increases the right rotation of dextrotartaric acid. The committee named cite the following parallel experiments:[3]

	Tartaric acid p	Boric acid p	Water q	d	l	t	α_r.	$[\alpha]_r$.
Levotartaric acid	23.89	4.76	71.35	1.13181	5.198	23.2	$-52.12°$	$-37.08°$
Dextrotartaric acid.	23.78	4.80	71.42	1.13158	5.1935	23.2	$+53.07$	$+37.97$

Salts of l-Tartaric Acid

l-Ammonium Tartrate, $(NH_4)_2C_4H_4O_6$.

Water $p = 12.16$, $t = 18.2$, $[\alpha]_j = -38.20$[4] from which by multiplication with $\frac{23}{30}$ we have $[\alpha]_r = -29.29$. For the *d*-salt Biot found $[\alpha]_r = +29.0$.

l-Sodium Ammonium Tartrate, $NaNH_4C_4H_4O_6 + 4H_2O$.

Water $p = 33.33$, $t = 16.5$, $[\alpha]_j = -26.0°$[5]

The solubility is the same as with the *d*-salt.

Levotartar Emetic, $KSbOC_4H_4O_6 + \frac{1}{2}H_2O$.

Water $p = 6.80$, $t = 19°$, $[\alpha]_j = -156.2°$. A similar solution of the *d*-salt gave $[\alpha]_j = +156.2°$.[6]

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[1] Ann. chim. phys., [3] 28, 77

[2] *Ibid.*, [3], 28, 101 to 105

[3] *Ibid.*, [3], 28, 110 to 112

[4] Pasteur. *Ibid.*, [3], 28, 84

[5] Pasteur. *Ibid.*, [3], 28, 90

[6] Pasteur. *Ibid.*, [3], 28, 87

l-Calcium Tartrate, $CaC_4H_4O_6 + 4H_2O$, dissolved in hyd chloric acid shows right rotation. A solution of 20 grams the salt in 63 cc of hydrochloric acid (containing 7.09 gra HCl) showed, for $l = 3.9$ dm., $\alpha_j = +6.7°$. If *d*-calciu tartrate is dissolved in hydrochloric acid the solution sho left rotation.[1]

Combinations of d- and l-Tartrates with d- and l-Malates

Right ammonium acid tartrate and left ammonium malat form a crystallizable combination which, when dissolved i aqueous ammonia, shows the same rotation as a mixture o equal molecules of the two salts.

$$c = 4, \quad [\alpha]_j = +14\,5°$$ [2]

d-Ammonium acid tartrate and *l*-ammonium acid malat form no combination with each other.

Combinations of *d*- and *l*-tartramide with *l*-malamide.

d-Tartramide, $[\alpha]_j = +133\,9°$.
l-Tartramide, $[\alpha]_j = -134.15°$, for $c = 1.305$.
l-Malamide, $[\alpha]_j = -47.5°$.

d-Tartramide and l-Malamide, dissolved in equal molecular proportions, yield an easily crystallizable compound:

d-Tartro-l-malamide, $[\alpha]_j = +43\,02°$.

l-Tartramide and l-Malamide, dissolved in equal molecular proportions, yield also a crystallizable compound which is more soluble than the last:

l-Tartro-l-malamide, $[\alpha]_j = -95.71°$ [3]

d-Tartaric acid forms with asparagin an easily crystallizable compound, but *l*-tartaric acid does not.[4]

l-Quinic Acid, $C_7H_{12}O_6$

1. Water,	$c =$	2	6	10
	$[\alpha]_D^{15} =$	-44.09	-43.84	$-43\,75$[5]

2. Water, $c = 8\,9$ to 53.03, $[\alpha]_D^{18} = -43\,8$ to 43.9.[6]
3. Water, $c = 1.57$ to 12.71, $[\alpha]_D^{16} = -45\,5$ to 45.7.[7]

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[1] Pasteur Ann. chim. phys, [3], 28, 78.
[2] Pasteur *Ibid*, [3], 38, 464
[3] Pasteur *Loc cit*, p 465
[4] Pasteur. *Loc cit*, p 437
[5] Hesse Ann Chem (Liebig), 176, 124.
[6] Eykman · Ber. d chem Ges., 24, 1297
[7] Oudemans Rec trav chim Pays-Bas, 4, 166

4. Water, $p = 9.93$ to 29.50, $[\alpha]^{20}_{D} = -43.47 - 0.0230p$.[1]

Quinates The rotation decreases somewhat with increasing dilution, and finally reaches nearly the same value for all.[2] See §61 Addition of free alkali produces an increase in the specific rotation in consequence of a decrease in the extent of dissociation.[3]

12. Acids with Seven Atoms of Oxygen

See the aldehydes under group 16 (oxyaldehydes, sugars).

d-GLUCONIC ACID (Dextronic acid, Maltonic acid), $CH_2OH.(CH\,OH)_4COOH = C_6H_{12}O_7$.

The free acid is a sirup, which by long standing over sulphuric acid is partly converted into the lactone, $C_6H_{10}O_6$; a complete conversion follows by prolonged heating to 100°.[4] On the reciprocal transformation of the acid and lactone in aqueous solution at the ordinary temperature see *Multirotation*, §75.

Calcium Salt, $Ca(C_6H_{11}O_7)_2 + H_2O$ (from dilute alcohol)

Water .... $c = 1.8176$, after 10 minutes $[\alpha]_D$ $+7.92°$
Water ...... $c =$ " " 1 hour " $+5.94°$ to $4.8°$

Exhibits multirotation.[5]

$Ca(C_6H_{11}O_7)_2 + 2H_2O$ (from water).

Water .... $c = 10$ (anhydrous), $[\alpha]^{20}_{D}$ $+6.66°$[6]
" .... c 10 " " $+7°$[7]

Shows no multirotation[8]

Anhydride, $C_6H_{10}O_6$. Crystals. Melting-point 130° to 135°.

Water ... p 8.32, d^{20} 1.032, t 20°, $[\alpha]_D = +68.2°$

At the end of twenty-four hours the rotation had fallen to 64.2°, but the solution had an acid reaction, evidently because free acid had been formed.[9]

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[1] Thomsen J prakt Chem., [2], **35**, 156.
[2] Oudemans *Loc cit*
[3] Thomsen: *Loc cit*
[4] Fischer. Ber d chem Ges., **23**, 2625
[5] Herzfeld Ann. Chem (Liebig), **220**, 345.
[6] Fischer · Ber d. chem. Ges, **23**, 2614
[7] Schnelle, Tollens
[8] Fischer
[9] Fischer Ber d. chem. Ges., **23**, 2626

l-Gluconic Acid. The mixture of acid and lactone rotates strongly to the left.[1]

Calcium Salt, $Ca(C_6H_{11}O_7)_2$ (dried over H_2SO_4). Needles.

Water...... $p = 10.298$, $d_4^{20} = 1.049$, $t = 20°$, $[\alpha]_D = -6.64°$ [2]

Anhydride. The rotation was determined in a hydrochloric acid solution of calcium gluconate.

$c = 6.9$ (anhydride), $t = 20°$, $[\alpha]_D = -22.0°$ [1]

d-Mannonic Acid, $C_6H_{12}O_7$.

Anhydride, $C_6H_{10}O_6$. From *d*-mannone by oxidation with bromine. Glittering needles. Melting-point 149° to 153°.

Water...... $p = 9.99$, $d_4^{20} = 1.0381$, $t = 20°$, $[\alpha]_D = +53.81°$ [3]

l-Mannonic Acid (Arabinose carboxylic acid).

Anhydride, $C_6H_{10}O_6$. From arabinose and hydrocyanic acid. Rhombic crystals which soften between 145° and 150°

Water........ $p = 9.1807$, $d = 1.0329$, $[\alpha]_D = -54.8°$ [4]

d-Gulonic Acid, $C_6H_{12}O_7$.

Anhydride, $C_6H_{10}O_6$. From *d*-saccharic acid by reduction. Trimetric crystals. Melting-point 178° to 180°.

Water.... $p = 10.219$, $d = 1.0373$, $t = 20°$, $[\alpha]_D = +55.1°$ [5]

From glucoronic acid

Water............ $c = 2.157$, $t = 19°$, $[\alpha]_D = +56.1°$ [6]
Calcium salt...... $[\alpha]_D = -14.45°$

l-Gulonic Acid (Xylose carboxylic acid)

Anhydride, $C_6H_{10}O_6$. From xylose and hydrocyanic acid. Trimetric prisms. Melting-point 185° (cor.).

Water. $p = 9.15$, $d = 1.034$, $t = 20°$, $[\alpha]_D = -55.3°$ [7]

d-Galactonic Acid, $C_6H_{12}O_7$.

On the multirotation of the free acid, separated from the calcium salt by aid of hydrochloric acid, through change into the lactone, see §75.

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[1] Fischer
[2] Fischer Ber d chem Ges, **23**, 2614
[3] Fischer, Hirschberger Ber d chem Ges, **22**, 3218
[4] Kiliani, *Ibid*, **19**, 3034
[5] Fischer, Piloty *Ibid*, **24**, 521
[6] Thierfelder Ztschr physiol Chem, **15**, 71
[7] Fischer, Piloty

Calcium Salt, $Ca(C_6H_{11}O_7)_2 + 5H_2O$. Monoclinic crystals.

Water + HCl, $c = 0.76°$, $t = 15°$, $[\alpha]_D =$ about $+ 2.85°$

But if the calcium salt is decomposed by oxalic acid, two crystalline substances result: 1, $C_6H_{12}O_7$ $(= C_6H_{10}O_6 + H_2O)$, with melting-point 65°, and 2, $C_6H_{10}O_6$, with melting-point 90° to 92°. The first is not the true galactonic acid, but the hydrate of the anhydride.[1]

TALONIC ACID, $C_6H_{12}O_7$. Made by heating *d*-galactonic acid, pyridine and water to 150°. The mixture of acid and anhydride is strongly left rotating.[2]

d-IDONIC ACID, $C_6H_{12}O_7$.

Double Salt, $(C_6H_{11}O_7)_2Cd + CdBr_2$.

$p = 11.14$, $d = 1.078$, $t = 20°$, $[\alpha]_D = + 3.41°$[3]

l-IDONIC ACID

Double Salt, $(C_6H_{11}O_7)_2Cd + CdBr_2$.

$p = 10.562$, $d = 1.076$, $t = 20°$, $[\alpha]_D = - 3.25°$[1]

RHAMNOHEXONIC ACID (Isodulcite carboxylic acid), $CH_3.(CH\,OH)_5.COOH = C_7H_{14}O_7$

Anhydride, $C_7H_{12}O_6$. Crystals. Melting-point 168°

Water .... $c = 10.034$, $t = 20°$, $[\alpha]_D = + 83.8°$

Shows no multirotation.[5]

l-TRIOXYGLUTARIC ACID, $C_5H_8O_7$.

By oxidation of arabinose with nitric acid. Microscopic plates. Melting-point 127°

Water . . $p = 9.59$, $d = 1.0441$, $t = 20°$, $[\alpha]_D = - 22.7°$

The rotation remained unchanged after twenty-four hours.[6]

Potassium Salt, $K_2C_5H_6O_7$. Monoclinic plates or prisms.

1 From rhamnose.

Water .... $p = 10.863$, $d_4^{20} = 1.0685$, $t = 16°$, $[\alpha]_D = + 9.35°$
" .... $p = 9.192$, " $= 1.0569$, $t = 13°$, " = 9.50
" .... $p = 29.498$, " $= 1.1935$, $t = 14°$, " = 9.58

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[1] Schnelle and Tollens Ann. Chem (Liebig), **271**, 82

[2] Fischer Ber. d. chem. Ges., **24**, 3623.

[3] Fischer, Fay: *Ibid*, **28**, 1982.

[4] Fischer, Fay. *Ibid.*, **28**, 1977

[5] Fischer, Piloty *Ibid.*, **23**, 3104

[6] Fischer: *Ibid*, **24**, 1836, 2686

2 From arabinose

Water . .... . $p = 3\ 0741$, $d_4^{20} = 1\ 0186$, $t = 19°$, $[\alpha]_D = +9\ 13°$

GLUCURONIC ACID, $COOH(CH.OH)_4\ CHO = C_6H_{10}O_7$

Potassium Salt, $KC_6H_9O_7$ (at 100°), needles.

Water... ...... $p = 3\ 85$, $t = 18°$, $[\alpha]_D = +21.25°$
" . . .. .. $p = 1\ 925$, $t = 18°$, " = 21.82

The specific rotation increases on dilution. The potassium salt rotates as strongly as does the amount of anhydride contained in it

Anhydride From euxanthinic acid. Monoclinic crystals. Melting-point 175° to 178° (with decomposition).

Water $p = 14\ 14$ $d^{18} = 1\ 06201$, $[\alpha]_D^{18} = +19.15°$
" ... " = 9 575, " = 1 04125, " = 19.26
" .... " = 7 719, " = 1 03307, " = 19.35
" . " = 7 07, " = 20 06
" . " = 4 787, " = 19 22
" " = 3 86, " = 19 89
" .. " = 3 54, " = 20 93
" . " = 2 39, " = 21 80
" ... " = 1 93, " = 21 66

Effect of temperature [2]

	p	$[\alpha]_D$ at			
		5°	18°	28°	34°
Water	14 14	+ 17 61°	+ 19 15°	+ 20 83°	+ 21 00°
"	9 575	17 63	19.26	20 37	21 10
"	7 719	17 72	19 35	20 47	21 27

Water . ... $c = 3$, $t = 21°$, $[\alpha]_D = 19\ 4°$ [3]

OXYGLUCONIC ACID, $C_6H_{10}O_7 + 2H_2O$. Sirup

Water .... $p = 2$, $[\alpha]_D = -14\ 5°$ [4]

SACCHARONIC ACID, $COOH\ C.OH\ CH_3(CH\ OH)_2.COOH = C_6H_{10}O_7$

Anhydride (Saccharon), $C_6H_8O_6 + H_2O$ Formed by the oxidation of saccharin with nitric acid Triclinic plates. Melting-point 156°

Water ... $p = 12\ 41$, $d = 1\ 0451$, $t = 18°$, $[\alpha]_D = -6\ 1°$ [5]

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[1] Will, Peters Ber d chem Ges, **22**, 1697
[2] Thierfelder Ztschr physiol Chem, **11**, 388
[3] Külz Ztschr f Biol, **22**, 478
[4] Boutroux Ann chim phys, [6], **21**, 565
[5] Kiliani Ber d chem Ges, **15**, 2959

13. Acids with Eight Atoms of Oxygen

LEVULOSECARBOXYLIC ACID,
$CH_2(OH).C(OH.COOH)(CH.OH)_3CH_2OH = C_7H_{14}O_8$.

Anhydride, plates or prisms, $C_7H_{12}O_7$. Softens at 126°; melting-point 130°.

Rotates strongly to the right in 6 per cent. aqueous solution.[1]

α-GLUCOHEPTONIC ACID (Dextrose carboxylic acid), $CH_2OH.(CH.OH)_5.COOH = C_7H_{14}O_8$.

Anhydride, $C_7H_{12}O_7$. Rhombic crystals.

Water . $p = 3.3817$, $d = 1.0144$, $t = 17.5°$, $[\alpha]_D = -55.3°$[2]

β-GLUCOHEPTONIC ACID

Anhydride, $C_7H_{12}O_7$. Colorless needles. Melting-point 151° to 152° (uncor.)

Water .. $p = 10.049$, $d = 1.0372$ $t = 20°$ Multirotation
After 20 minutes .... $[\alpha]_D = -79.1°$
After 24 hours constant .... " $= -67.7$

The multirotation is not caused here, as with the other lactones, by transformation into the acid, since at the end of the experiment the solution is found perfectly neutral.[3]

d-GALACTOSECARBOXYLIC ACID, $CH_2OH.(CHOH)_5CO_2H$. Small needles; melting-point 145°.

The rotation of aqueous galactose solutions, to which hydrocyanic acid has been added in excess at the ordinary temperature, decreases gradually, and finally becomes 0. The amide of galactose carboxylic acid is formed, which on boiling with water is decomposed.

The acid is inactive in 5 per cent. aqueous solution ($l = 2$ dm.)[4]

Barium Salt, $Ba(C_7H_{13}O_8)_2$. From the amide on boiling with baryta water.

Water.............. $c = 12.01$, $t = 20°$, $[\alpha]_D = -5.50°$

d-MANNOHEPTONIC ACID (Mannose carboxylic acid), $CH_2OH.(CH.OH)_5.COOH$. Melting-point 175°. Rotates slightly to the left in aqueous solution.

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[1] Kiliani: Ber. d. chem. Ges., **19**, 1915.
[2] Kiliani: Ibid., **19**, 770.
[3] Fischer: Ann. Chem. (Liebig), **270**, 84.
[4] Maquenne: Compt. rend., **106**, 286.

Anhydride, $C_7H_{12}O_7$. Crystals. Melting-point 148° to 150°.

Water............ $c = 10.009$, $t = 20°$, $[\alpha]_D$ 74.23°

Slight decrease later.[1]

l-MANNOHEPTONIC ACID.

Anhydride, $C_7H_{12}O_7$. Crystals. Melting-point 153° to 155°. From *l*-mannose by the cyanhydric reaction and saponification.

Water .. $p = 5.27$, $d_4^{20} = 1.02$, $t = 20°$, $[\alpha]_D$ + 75.15°[2]

RHAMNOHEPTONIC ACID, $CH_3(CHOH)_6.COOH$. From rhamnohexose by hydrocyanic acid.

Anhydride, $C_8H_{14}O_7$. Crystals. Melting-point 160°.

Water............ $c = 10.036$, $t = 20°$, $[\alpha]_D$ + 55.6°

After six hours the rotation was still unchanged.

Saccharic Acids, $CO_2H.(CHOH)_4.CO_2H = C_6H_{10}O_8$.

d-SACCHARIC ACID.

Anhydride, *Lactone*, $C_6H_8O_7$. Needles. Melting-point 130° to 132°.

The right rotation observed by Clerget[3] has been confirmed by Sohst and Tollens.[4] The latter found that aqueous solutions of the anhydride exhibit increased rotation; but if the saccharic acid is thrown out from its solutions by aid of acids the phenomenon of decreasing rotation is noticed. In both cases a constant value of about 22.5° is reached, in the one instance by a gradual decrease, and in the other by a gradual increase in rotation See §75.

The observations of Sohst and Tollens on the gradual change of the specific rotation of saccharic acid have been already given in §75.

Acid Ammonium Salt, $NH_4C_6H_9O_8$.

Water........ $c = 20.029$, $[\alpha]_D = + 5.84°$

Multirotation could not be detected.[5]

The specific rotation of *l*-saccharic acid has not yet been determined. Its crystalline potassium salt, $KC_6H_9O_8$, rotates slightly to the left [1]

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[1] Fischer, Passmore Ber. d. chem Ges, **23**, 2226.

[2] Smith Ann Chem. (Liebig), **272**, 183

[3] Compt. rend, **53**, 343

[4] Ann Chem. (Liebig), **245**, 9.

[5] Sohst and Tollens *Ibid.*, **245**, 15.

ISOSACCHARIC ACID Rhombic crystals. Melting-point 185°.

Water.. $p = 4.266$, $d_4^{20} = 1.01689$ $t = 20°$ $[\alpha]_D = +46.12°$

The specific rotation of the aqueous solution is not changed even after heating three hours to 200° to 220° [2]

Water.......... $p = 4.7$ after heating, $[\alpha]_D = +48.93°$ [3]

Isosaccharic Acid Diethyl Ester, $(C_2H_5)_2C_6H_8O_8$. Crystals. Melting-point 73° ; boiling-point 250°.

Water .. .. $c = 5$, $[\alpha]_D = +35.5°$ [4]

Isosaccharic Acid Diamide, $C_6H_6O_5(NH_2)_2$, Crystals. Melting-point 226°.

Water .... $c = 5$, $[\alpha]_D = +7.16°$ [4]

NORISOSACCHARIC ACID, $(C_6H_{10}O_8)$. Calcium salt ($p = 5$) and HCl. After heating

$[\alpha]_D = +51.73°$ [5]

d-MANNOSACCHARIC ACID

Anhydride, $C_6H_6O_6 + 2H_2O$. Crystals Melting-point 180° to 190°. In fresh aqueous solution :

$p = 3.432$, $d = 1.0176$, $t = 23°$, $[\alpha]_D = +201.8°$ [6]

MUCIC ACID, $(CHOH)_4(CO_2H)_2$ Crystals. Melting-point 213°. This acid is inactive from the symmetrical arrangement of its molecule, and former observations of rotation must be referred to impurities.[7] For this reason the efforts of Ruhemann and Dufton[8] to split up the acid into two active components by aid of quinine, cinchonine, or strychnine failed.

TALOMUCIC ACID, $C_6H_{10}O_8$. Microscopic plates Melting-point 158° (with decomposition).

For freshly prepared aqueous solutions, $p = 3.84$, $d = 1.0172$,

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[1] Fischer. Ber. d. chem Ges, **23**, 2621.

[2] Tiemann and Haarmann. *Ibid*, **19**, 1260

[3] Tiemann *Ibid.*, **27**, 137.

[4] Tiemann and Haarmann.

[5] Tiemann. Ber. d chem. Ges., **27**, 137

[6] Fischer *Ibid.*, **24**, 539.

[7] Fischer, Hertz *Ibid.*, **25**, 1247.

[8] J Chem. Soc., **59**, 750.

$t = 20°$, $[\alpha]_D =$ about 29.4° On heating the solution, the rotation diminishes on account of lactone formation.[1]

14. Acids with Nine Atoms of Oxygen

α-GLUCOOCTONIC ACID, $CH_2OH(CH.OH)_6\ COOH = C_8H_{16}O_9$

Anhydride (From *α*-glucoheptose), $C_8H_{14}O_8$ Melting-point 145° to 147° (uncor).

Water · $p = 10\ 405$, $d = 1.0417$, $t = 20°$, $[\alpha]_D = + 45\ 9°$ [2]

β-GLUCOOCTONIC ACID

Anhydride. By product in the formation of the *α*-acid. Crystals; melting-point 186° to 188° (uncor).

Water... $p = 11\ 399$, $d = 1\ 042$, $t = 20°$, $[\alpha]_D = + 23\ 6°$

The rotation remained unchanged after twelve hours [3]

d-MANNOOCTONIC ACID, $C_8H_{16}O_9$.

Anhydride, $C_8H_{14}O_8$. From mannoheptose. Crystals, melting-point 167° to 170°

Water · $p = 9\ 8534$, $d_4^{20} = 1.0394$, $t = 20°$, $[\alpha]_D = - 43\ 58°$ [4]

RHAMNOOCTONIC ACID, $CH_3(CH.OH)_7\ COOH = C_9H_{18}O_9$.

Anhydride, $C_9H_{16}O_8$. From rhamnoheptose. Needles Melting-point 171° to 172°.

Water.. $p = 4\ 762$, $d = 1.0163$, $t = 1\ 0163$, $t = 20°$, $[\alpha]_D = - 50\ 8°$ [5]

GALAOCTONIC ACID, lactone, $C_8H_{14}O_8$. Melting-point 220° to 223°

$p = 4\ 26$, $d = 1.017$, $t = 20°$, $[\alpha]_D = + 64.0°$ [6]

α-PENTOXYPIMELIC ACID, $COOH(CH\ OH)_5\ COOH = C_7H_{12}O_9$ From *α*-glucoheptonic acid

The anhydride $C_7H_{10}O_8$ is inactive in 10 per cent aqueous solution.[7]

β-PENTOXYPIMELIC ACID. From *β*-glucoheptonic acid

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[1] Fischer Ber d chem Ges, **24**, 3622

[2] Fischer Ann Chem (Liebig), **270**, 92

[3] Fischer *Ibid*, **270**, 100

[4] Fischer, Passmore Ber d chem Ges, **23**, 2233

[5] Fischer, Piloty *Ibid*, **23**, 3109

[6] Fischer Ann Chem (Liebig), **288**, 149

[7] Fischer *Ibid*, **270**, 90

Anhydride, $C_7H_{10}O_8$ Crystals Melting-point about 177°.

Water .... $p = 9.972$, $d = 1.0433$, $t = 20°$, $[\alpha]_D + 68.5°$ [1]

TANNIC ACID, TANNIN, $C_{14}H_{10}O_9 + 2H_2O$.

Water .. $p = 1$, $t = 20°$, α_D (for 2 dm) $= + 1.50°$ (?)[2]

This acid was formerly supposed to be inactive, but Günther and also H. Schiff[3] recognized it as strongly right rotating. The latter found for pure commercial preparations in aqueous solutions with $c = 1$, a rotation varying from $[\alpha]_D = + 14°$ to $+ 67°$ for different preparations. This stands in contradiction to the constitutional formula proposed by Schiff for tannin, according to which there is no asymmetric carbon atom present, and which is supported by the fact that the synthetic tannin obtained from gallic acid is optically inactive, also by the fact that the products obtained from natural tannin by hydrolysis with weak hydrochloric acid (gallic acids) are likewise inactive. To clear up this point, Walden[4] has undertaken some experiments on the separation of different components from commercially pure tannin ($[\alpha]_D = + 67.5°$, in water, $c = 1$) by means of dialysis, and also by fractional precipitation from solutions in ethyl acetate by addition of benzene, etc. By such methods he found it possible to separate the tannin into fractions with unequally strong rotations. Walden, therefore, considers it probable that the rotating power of the natural tannin is due to admixture with small amounts of highly active substances of unknown composition.

Rosenheim and Schidrowitz[5] have also examined the acid anew and come to conclusions somewhat opposed to Walden's. They conclude that the larger portion of the commercial acid is a single homogeneous body of high rotation, and that the formula of Schiff must be wrong.

15. Acids with Ten Atoms of Oxygen

α-GLUCONONONIC ACID, $C_9H_{18}O_{10}$. From α-glucooctose.

Anhydride, $C_9H_{16}O_9$. Has not been obtained crystalline.

Water .... $c =$ about 10, $t = 20°$, $[\alpha]_D = + 33°$ [6]

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[1] Fischer. *Loc. cit.*

[2] Günther. Ber. d. deutsch. Pharm. Ges., **5**, 297, 1895.

[3] Chem. Ztg., (1895), p. 1680; (1896), p. 865.

[4] Ber. d. chem. Ges., **30**, 3151 (1897).

[5] J. Chem. Soc., **73**, 878.

[6] Fischer. Ann. Chem. (Liebig), **270**, 102.

d-MANNONONONIC ACID, $C_9H_{18}O_{10}$. From mannooctose.

Anhydride, $C_9H_{16}O_9$. Crystals; melting-point 175° to 177°.

Water .... $c = 10.002$, $t = 20°$, $[\alpha]_D = -41.0°$[1]

16. Oxyaldehydes, Aldoses, Aldehyde Sugars

ARABINOSE, $CHO.(CH.OH)_3.CH_2OH = C_5H_{10}O_5$.

d-Arabinose. Formed by degradation of *d*-glucose. Rhombic crystals.

Water . .. $p = 10.11$, $d^{20} = 1.0402$, $t = 20°$, $[\alpha]_D = -104.1°$

Compound of d-Arabinose with Acetamide, $CH_2OH.(CHOH)_3CH(NH\ C_2H_3O)_2$. Fine white needles; melting-point 187°.

Water. ... $p = 10.03$, $d^{20} = 1.0455$, $t = 20°$, $[\alpha]_D = -9.5°$[2]

l-Arabinose. From cherry gum, exhausted beet cuttings, exhausted beermash, wheat bran, gum arabic, gum tragacanth, quince mucilage, gedda mucilage, etc. Glittering trimetric prisms,[3] melting-point 160°,[4] 152° to 153°;[5] 158° to 160°[6]

Water.. .	$c = 10$,	$t = 5°$,	$[\alpha]_D = +104.4°$[7]
Water.....	$c = 10$,	$t = 18$,	“ $= +104.4°$[8]
Water... .	$c = 10.369$,	$t = 20$,	“ $= +105.4°$, $[\alpha]_j = +118°$[9]
Water..	$c = 8.740$,		“ $= +105.1°$[10]
Water .. .	$c = 9.730$,	$t = 20$,	“ $= +104.55°$[11]
Water.. ..	$c = 10.201$,	$t = 20$,	“ $= +104.64°$[11]
Water	$c = 9.016$,	$t = 20$,	“ $= +103.87°$[12]

l-Arabinose exhibits the phenomenon of multirotation. The beginning rotation for $c = 9.73$ is about 157°.[13] See §72. Ammonia immediately destroys the multirotation.[14] The rotation decreases with increasing temperature. For example:

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[1] Fischer, Passmore. Ber. d. chem. Ges., **23**, 2236.

[2] Wohl. *Ibid.*, **26**, 740.

[3] O'Sullivan. J. Chem. Soc., **45**, 41.

[4] Scheibler. Ber. d. chem. Ges., **1**, 108; v. Lippmann. Ber. d. chem. Ges. **17**, 2239.

[5] Frankland, MacGreger. J. Chem. Soc., **61**, 737.

[6] Conrad, Guthzeit. Ber. d. chem. Ges., **18**, 2907.

[7] Bauer. *Ibid.*, **22**, Ref. 835.

[8] Scheibler. *Ibid.*, **17**, 1731.

[9] v. Lippmann. *Ibid.*, **17**, 2239.

[10] Kiliani. *Ibid.*, **19**, 3031.

[11] Parcus, Tollens. Ann. Chem. (Liebig), **257**, 173.

[12] Allen, Tollens. *Ibid.*, **260**, 300.

[13] Parcus and Tollens. *Loc. cit.*

[14] Schulze, Tollens. Ann. Chem. (Liebig), **271**, 49.

$$[\alpha]_D^{13} = +106.0^\circ, \quad [\alpha]_D^{20} = +104.5^\circ\ ^{1}$$

Arabinosazone, $C_5H_8O_3(N.NHC_6H_5)_2$. Crystals; melting-point 157° to 158°;[2] 159°.[3]

Alcohol, 95 per cent ... $c = 3.40$, $t = 20^\circ$, $[\alpha]_D = +18.90^\circ$

The rotation gradually disappears[4] Compare Fischer.[5]

i-Arabinose An aqueous solution which contained 10 per cent. of each of the active components rotated in a 1 dm. tube, after fifteen minutes, 4° to the right; after one hour + 0.2°, and after two hours it was inactive. Wohl[6] refers this to the birotation of the *l*-arabinose

XYLOSE, $CH_2OH(CHOH)_3CHO = C_5H_{10}O_5$. White needles or orthorhombic prisms; melting-point 144° to 145°.

Water .. $c = 10.664$, $t = 20^\circ$, $[\alpha]_D = +19.31^\circ$ }[7]
Water .. $c = 11.070$, $t = 20$, " $= +19.22$ }
Water .. $c = 10.108$, $t = 22$, " $= +19.39$
Water .. $p = 9.940$, $d_4^{20} = 1.0359$, $t = 20^\circ$, $[\alpha]_D + 18.99^\circ$[8]
(Mean of about 50 readings.)

The effect of concentration on the specific rotation of aqueous solutions of xylose was investigated by Schulze and Tollens[9] All the solutions were tested after standing twenty to twenty-four hours, the 61 per cent. solution after a quarter of an hour.

p	d_4^{20}.	$[\alpha]_D^{20}$.
3.115	1.00977	+ 18.425°
5.376	1.01814	18.547
9.706	1.03481	18.773
21.744	1.08299	19.610
34.355	1.13750	20.495
46.395	1.19266	21.429
56.229	1.24205	22.681
61.747	1.27258	23.702

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[1] Parcus, Tollens.

[2] Scheibler

[3] Allen and Tollens.

[4] Allen and Tollens Ann. Chem (Liebig), **260**, 300

[5] Fischer: Ber. d chem. Ges., **23**, 385, note.

[6] *Ibid*, **26**, 740

[7] Parcus and Tollens: Ann Chem. (Liebig), **257**, 175.

[8] Wheeler, Tollens: *Ibid*, **254**, 310

[9] *Ibid.*, **271**, 40.

From these figures, interpolation formulas for the temperature of 20° may be calculated.

I....... $c = 3$ to 34, $[\alpha]_D = 18.095 + 0.06986\,p$,
II....... $c = 34$ to 61, " $= 23.089 - 0.1827\,p + 0.00312\,p^2$

The temperature has no marked effect on the rotation between 15° and 20°, but above 20° a change takes place which must be considered in any exact investigations.

Water..... $p = 10.0829$, $d_4^{20} = 1.0362$

t	$[\alpha]_D$.
15°	+ 18.898°
20	18.909
25	19.248
30	19.628

Xylose exhibits multirotation. §72.

Observations of Wheeler and Tollens[1] gave:

Water .. $c = 10.236$, $t = 20°$, after 5 minutes $[\alpha]_D = + 85.86°$
Water . $c = 10.236$, $t = 20$, " 10 " " $= + 70.14$
Water .. $c = 10.236$, $t = 20$, " 16 hours constant " $= + 18.59$

Parcus and Tollens[2] found the beginning rotation lower

Water ..... $c = 10.664$, $t = 20°$ after $5\frac{1}{2}$ minutes $[\alpha]_D = + 77.87°$
constant " 24 hours " $= + 19.31$
Water ...... $c = 11.070$, $t = 20°$, " $4\frac{1}{2}$ minutes " $= + 78.61$
constant " 24 hours " $= + 19.22$

From this $[\alpha]_D$ two minutes after solution = about 91°
" " " immediately " " = about 100

Ammonia of about 0.1 per cent strength brings about the end rotation immediately. If more than 0.1 per cent. is present the rotating power is very greatly decreased. See §73.[3]

Xylosazone, $C_5H_8O_3(N_2H.C_6H_5)_2$. Bright yellow silky needles; melting-point 159° to 160°

Alcohol, 95 per cent . ... $p = 2.815$, $d = 0.85$, $[\alpha]_D = - 43.36°$

After more than a week the solution showed approximately the same end rotation.[4]

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[1] Ann Chem (Liebig), **254**, 311
[2] *Ibid*, **257**, 175
[3] Schulze, Tollens *Ibid*, **271**, 49
[4] Allen, Tollens *Ibid*, **260**, 295

FUCOSE, $CH_3(CHOH)_4CHO = C_6H_{12}O_5$. From sea weeds. Crystals; melting-point 116° to 140°.

Water.. $c = 9.1375$ (dried at 65°), $t = 20°$, $[\alpha]_D = -75.96°$

Fucose shows marked multirotation. An aqueous solution clarified with alumina cream gave the following rotations:[1]

$c = 6.9155$, $t = 20°$, after 11 minutes $[\alpha]_D = -111.8°$
" 14 " " = 106.8
" 21 " " = 97.8
" 31 " " = 90.0
" 71 " " = 79.0
" 101 " " = 77.8
" 146 " " = 76.8
On the following day constant = − 77.0

RHAMNOSE (Isodulcite, rhamnodulcite), $CH_3(CHOH)_4CHO + H_2O = C_6H_{12}O_5 + H_2O$.

Ordinary Rhamnose Monoclinic crystals; melting-point 93° to 94° (On the three modifications of the substance, see §72.) The following numbers hold for the final constant rotation and the hydrate:

From quercitrine, water...... $c = 18.076$, $t = 17°$, $[\alpha]_D = +8.04°$[2]
From xanthorhamnine, water $c = 26.04$, $t = 17°$, $[\alpha]_D = +8.07°$[3]
From xanthorhamnine, water $c = 12.390$, $t = 18°$, $[\alpha]_D = +8.83°$[4]
From naringenine (citrus decumana) water............ $c = 25.166$, $t = 17°$, $[\alpha]_D = +8.2°$[5]

Effect of concentration

$c =$	5	9	18	22	40
$[\alpha]_D =$	+8.48°,	+8.52°,	+8.50°,	+8.51°,	+8.65°

The rotation is, therefore, influenced but little by the concentration. With elevation of temperature, the rotation decreases and *vice versa* For $t = 6°$ to 20° this formula holds.

$$[\alpha]_D = 9.18° - 0.035\, t$$ [6]

Rhamnose exhibits multirotation as described in §72. Freshly prepared solutions show left rotation which changes gradually to right rotation:[7]

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[1] Günther Tollens. Ann Chem. (Liebig), **271**, 86

[2] Berend: Ber d chem. Ges., **11**, 1354.

[3] Liebermann, Hörmann *Ibid.*, **11**, 956. Will: *Ibid.*, **20**, 1186

[4] Stohmann, Langbein. J. prakt Chem., [2], **45**, 308

[5] Will Ber. d. chem. Ges., **20**, 294.

[6] Schnelle, Tollens: Ann Chem (Liebig), **271**, 62

[7] Jacobi: *Ibid.*, **272**, 175

Water……. $p = 10$, $d_4^{20} = 1.0236$, $t = 20°$

After 1 minute. ……………………… $[\alpha]_D = -5.6°$

After 8 minutes……… ……………… " $= 0.0$

Constant after 1 hour ………………… " $= +8.3$

Water ……….. $c = 10$, $t = 19.5$ to $20.5°$

After $5\frac{1}{2}$ minutes……….. ………….. $[\alpha]_D = -3.11°$

After $9\frac{1}{2}$ minutes……………………… " $= 0.0$

Constant after 57 minutes.. ………….. " $= +8.56$

In another series of experiments, the beginning rotation was —4.5°.[1]

The decrease in rotation takes place regularly with gradually diminishing rapidity.[2]

When rhamnose is heated to the melting-point, the end rotation is reached immediately.[3]

A small addition of ammonia destroys the multirotation[4]

Water, $c = 10.052$ $t = 20°$, $[\alpha]_D$ after 20 hours $= +7.86°$

Water with 0.1 per cent ammonia, $t = 20°$, $[\alpha]_D$ after 7 min $= +7.95$

For further observations on rhamnose see Gernez[5] and Tanret.[6]

On the rotation of rhamnose in alcoholic solution, see §64.

Anhydrous, Amorphous Rhamnose, Isodulcitan, $C_6H_{12}O_5$.

Water. …… .. . $p = 9.238$, $d = 1.0281$, $t = 20°$, $[\alpha]_D = +8.7°$

This shows no multirotation in water solution.[3]

Water .. ….. $p = 27.982$, $d_4^{20} = 1.1002$, $t = 20°$, $[\alpha]_D = +6.36°$

Water .. .. $p = 21.519$ " $= 1.0765$, $t = 20$, " $= +9.43$

Water …. … $p = 14.419$, " $= 1.0507$, $t = 20$, " $= +9.34$

Methyl alcohol (97.94 p. c.), $p = 19.06$, $d_4^{20} = 0.8842$, $[\alpha]_D = -10.59$

In alcoholic solution the rotation may be either + or — according to the concentration and the percentage of water in the alcohol. Rayman and Kruis[7] obtained the following numbers:

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[1] Schnelle and Tollens: *Loc cit.*

[2] Parcus and Tollens Ann Chem (Liebig), **257**, 160

[3] Jacobi

[4] Schulze, Tollens: Ann Chem (Liebig), **271**, 49

[5] Compt rend, **121**, 1150.

[6] *Ibid*, **122**, 86

[7] Bull soc chim, [2], **48**, 635

Ethyl alcohol	(5.31 p. c.),	p = 17.579,	d_4^{20} = 1.0534,	$[\alpha]_D$ = + 8.96°
" "	(10.91 " ")	16.694	1.0432	+ 8.18
" "	(29.84 " ")	17.690	1.0170	+ 4.14
" "	(43.57 " ")	18.621	0.9960	+ 3.28
" "	(38.27 " ")	11.177	0.9767	+ 2.35
" "	(66.09 " ")	12.669	0.9482	+ 0.84
" "	(94.00 " ")	10.445	0.8502	— 9.23
" "	(96.11 " ")	7.028	0.8292	— 10.04
" "	(97.36 " ")	4.875	0.8159	— 10.69
" "	(99.33 " ")	9.368	0.8176	— 10.65

Rhamnose Oxime, $C_6H_{12}O_4 \cdot NOH$. Crystals ; melting-point 127° to 128°. Does not show multirotation. See §72.

Rhamnose Phenylhydrazone, $C_6H_{12}O_4.(N_2H.C_6H_5)$. Colorless scales ; melting-point 159°. Dissolved in water by gentle heat and quickly cooled:

$p = 1.011$, $d_4^{20} = 1.0091$, $t = 20°$, $[\alpha]_D = + 54.3°$[1]

It does not show birotation. The rapidity of hydrazone formation may be followed by the polariscope.[2]

GALACTOSE, (Lactoglucose), $CH_2.OH.(CH.OH)_4.CHO$.

d-Galactose Found in three modifications. See §72.

Ordinary Galactose. Granular crystals ; melting-point 168° ;[3] 161° to 162°,[4] 162°.[5]

For the constant form there has been found :

Water, c = 10 to 15°, $[\alpha]_D$ = + 81.4 to 81.7°[6]
Water, p = 10, d^{18} = 1.0385, t = 18°, $[\alpha]_D$ = + 81.2°[7]
Water, c = 9.973, t = 15°, $[\alpha]_D$ = + 81.01°[8]
Water, p = 10.182, d_4^{20} = 1.0395, t = 20.5°, $[\alpha]_D$ = + 80.5°[9]
Water, p = 10, d^{20} = 1.0379, t = 20°, $[\alpha]_D$ = +81.5°, $[\alpha]_j$ = + 92.0°[10]

From β-galactan

Water.......... c = 10.078, t = 15°, $[\alpha]_D$ = + 81.54°[11]

For the dependence of the specific rotation of aqueous solutions on the percentage strength and temperature, Meissl h found[1]

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[1] Fischer, Tafel Ber. d. chem. Ges., **20**, 2574
[2] Jacobi. Ann. Chem. (Liebig), **272**, 174
[3] v. Lippmann. Ber. d. chem. Ges., **18**, 3335.
[4] Müntz. Jahresber., 1882, p. 1125
[5] Schulze, Steiger: Land. Vers. Stat., **36**, 423
[6] Kent, Tollens: Ber. d. chem. Ges., **17**, 668
[7] Scheibler *Ibid.*, **17**, 1731.
[8] Steiger. Ztsch. physiol. Chem., **11**, 373.
[9] Tollens, Stone Ber. d. chem. Ges., **21**, 1573
[10] v. Lippmann *Ibid.*, **17**, 2239.
[11] Schulze, Steiger: Land. Vers. Stat., **36**, 423.

$$[\alpha]_D^t = 83\ 883 + 0\ 0785\, p - 0.209\, t,$$

which formula holds for $p = 5°$ to $35°$ and $t = 10°$ to $30°$.

Rindell[2] gives the formula

$$[\alpha]_D^t = 83.037 + 0.199\, p - (0.276 - 0.0025\, p)\, t,$$

holding for $p = 11°$ to $20°$ and $t = 4°$ to $40°$.

The two formulas lead to the following specific rotations :

$p =$	10			15			20		
$t =$	10°	20°	30°	10°	20°	30°	10°	20°	30°
$[\alpha]_D$ Meissl	82 58	80 49	78.40	82.97	80 88	78 79	83.36	81.27	79.1
$[\alpha]_D$ Rindell	82.52	80 01	77 50	83 64	81.25	78.87	84 76	82.50	80 24

Galactose possesses multirotation. For the beginning rotation Meissl found 130° to 140°, v Lippmann 134.5°, Koch 132.5°, 133.8°, 137.4°. Parcus and Tollens[4] give the following observations :

$c = 11.0810$ $t = 20°$		$c = 10\ 2045$ $t = 20°$.	
Time after solution	$[\alpha]_D$	Time after solution	$[\alpha]_D$
7 minutes	117.23°	7 minutes	117 48°
8 "	116.14	8 "	116 47
10 "	114.27	10 "	114 43
20 "	107.71	20 "	107 31
30 "	102 87	30 "	102.40
40 "	98 81	40 "	98.33
50 "	95.88	50 "	94 26
1 hour	93 35	1 hour	91.72
2 hours	83.99	2 hours	83.58
4 "	81.02	3 "	81 37
5 "	80.55	7 " 24 "	80 27
6 " 7 " 24 "	80.39		

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[1] J. prakt Chem , [2], 22, 97

[2] Scheibler's N Z. Rbz -Ind , 4, 170.

[3] Pharm Ztg. f Russl , 1886

[4] Ann Chem (Liebig), 257, 168

From the curve constructed from this we have:

$[\alpha]_D$ after 2 minutes = about 122°
" at moment of solution = " 127°

0.1 per cent ammonia destroys the multirotation.[1]

d-Galactose Oxime, $C_6H_{12}O_5 \cdot NOH$. Crystals; melting-point, 175° to 176°. Multirotation shown.

Water .... $p = 5\ 1056$, $d_4^{20} = 1\ 017$, $t = 20°$
After 10 minutes............ $[\alpha]_D = +20\ 6°$
" 20 hours constant...... " $= +14.75$

On account of the slight solubility in cold water, solutions up to a strength of 5 per cent. only could be investigated.[2]

d-Galactose Phenylhydrazone, $C_6H_{12}O_5:(N_2H.C_6H_5)$. Crystals; melting-point, 158°

Dissolved by aid of gentle heat in water and quickly cooled:

$p = 1\ 980$ $d_4^{20} = 1.0065$, $t = 20°$, $[\alpha]_D = -21.6°$

Multirotation could not be observed.[3] See also Fischer and Tafel.[4]

d-Galactose Anilide, $C_6H_{11}O_5\ NH.C_6H_5$ Triclinic crystals; melting-point about 147°.

Ethyl alcohol (90 vol. per cent)
$p = 2\ 289$, d_4^{20} $0\ 8366$, $t = 20°$ to $23°$, $[\alpha]_D = -31\ 33°$
$p = 2.099$, " $0\ 8334$, $t = 20°$ to $23°$, " $= -31.44°$
Methyl alcohol ($d_4^{20} = 0\ 7907$)
$p = 1\ 699$, $d_4^{20} = 0.7997$, $t = 20°$ to $23°$, $[\alpha]_D = -33\ 12°$

d-Galactose-p-toluide, $C_6H_{11}O_5\ HN(CH_3)\ C_6H_4$ Crystals; melting-point, 139°.

Methyl alcohol (as above)
$p = 0.6167$, d_4^{20} $0\ 7952$, $t = 20°$ to $23°$, $[\alpha]_D = -33\ 99°$
Ethyl alcohol (50 per cent)
$p = 0\ 9832$, d_4^{20} $0\ 9316$, t $20°$ to $23°$, $[\alpha]_D = -10\ 91°$[5]

d-Galactose Pentaacetate, $C_6H_7O_6(C_2H_3O)_5$. Glistening rhombic plates; melting-point, 142°. Right-rotating[6]

l-Galactose. Formed in the fermentation of *i*-galactose by

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[1] Schulze, Tollens Ann. Chem. (Liebig), **271**, 49
[2] Jacobi Ber d chem. Ges., **24**, 698.
[3] Jacobi. Ann. Chem. (Liebig), **272**, 173.
[4] Ber. d. chem Ges., **20**, 2568
[5] Sorokin J. prakt. Chem., [2], **37**, 295 and 309
[6] Fudakowsky; Ber. d. chem Ges., **11**, 1071

beer yeast. Crystals; melting-point, 162° to 163° (not co
Exhibits multirotation.

Water.......... $c = 10$; $[\alpha]_D$ after 8 minutes $-$ 120°
" constant $= -$ 73.6°

These values may be looked upon as approximate only
the preparation used was not sufficiently pure.[1]

Sorbin (Sorbinose, sorbose), $CH_2OH.(CH.OH)_3.C$
CH_2OH. Rhombic crystals.

Water.......... $c = 23$, $[\alpha]_D$ $-46.9°$[2]
" .... $c = 9.957$, $[\alpha]_D = -43.4°$[3]

Shows no birotation.

Glucose (Glycose)

d-Glucose (Dextrose, grape-sugar, starch sugar), CH_2OI
$(CHOH)_4CHO + H_2O$. On the three modifications of *d*-gluco
see §72, p. 260.

Ordinary Glucose. Hydrated: monoclinic crystals; anh
drous. rhombic hemihedral. The constant specific rotati
of *d*-glucose has been determined by many observers. T
most reliable determinations in respect to purity of substan
as well as to accuracy in measurements, are those of Tollen
and they have shown that the specific rotation increases to a
appreciable extent with the percentage amount of glucose
in the solution. The increase may be expressed by the follow
ing formulas[5] which hold from the weakest to the stronge
solutions

I. *Anhydrous Glucose*, $C_6H_{12}O_6$. $t = 17°$

$$[\alpha]_D = 52.50 + 0.018796\,p + 0.00051683\,p^2$$
$$= 59.55 - 0.12216\,q + 0.0005168\,q^2$$

II. *Hydrated Glucose*, $C_6H_{12}O_6 + H_2O$.

$$[\alpha]_D = 47.73 + 0.015534\,p + 0.0003883\,p^2$$

According to this, we have the following specific rotation
for solutions containing different amounts of anhydrous glu
cose:

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[1] Fischer, Hertz Ber d chem Ges, **25**, 1247.

[2] Berthelot Ann chim phys, [3], **35**, 222.

[3] Wehmer, Tollens Ann Chem (Liebig), **243**, 320.

[4] Ber d chem Ges, **9**, 487, 1531, **17**, 2234

[5] *Ibid*, **17**, 2238

$p =$	5	10	15	20	25	30
$[\alpha]_D =$	52.61	52.74	52.90	53.08	53.29	53.53°
$p =$	35	40	50	60	70	80
$[\alpha]_D =$	53.79	54.08	54.73	55.49	56.35	51.31°

Compare with reference to this, Ost,[1] and the reply of Tollens.[2]

Solutions freshly prepared, without heat, show birotation (see §72). Among the many experiments on the change in the rotation of glucose, it will be sufficient to quote those of Parcus and Tollens as the most exact.[3] These were made with glucose, prepared according to Soxhlet's method from cane-sugar, and dried at 60° to 70°.

$t = 20°$, $c = 9.0970$		$t = 20°$, $c = 5.5255$	
Time after solution	$[\alpha]_D$	Time after solution	$[\alpha]_D$
5½ minutes	105.16°	7 minutes	104.26°
6½ "	104.59	8 "	103.64
10 "	101.55	9 "	103.01
12 "	100.03	10 "	102.38
14 "	97.94	12 "	101.13
20 "	92.42	13 "	100.50
30 "	83.86	14 "	99.88
50 "	72.26	15 "	98.63
1 hour	68.27	25 "	92.35
1¼ hours	63.33	30 "	88.61
1½ "	59.71	1 hour	73.58
6 " constant	52.49	7 hours, constant	52.60

The end rotation appears immediately when the glucose has been heated to melting,[4] or when the solution is heated for some time.[5] The addition of 0.1 per cent. of ammonia destroys the multirotation,[6] but if more ammonia is added the specific rotation is much decreased

$c =$ about 10, $t = 20°$: Directly after solution $[\alpha]_D = 49.82°$
After 30 minutes " $= 50.00$
After 1½ hours " $= 49.65$
After 24 hours " $= 46.36$

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[1] Ber. d. chem. Ges., **24**, 1641.
[2] *Ibid.*, **24**, 2000.
[3] Ann. Chem. (Liebig), **257**, 164.
[4] Schmidt: *Ibid.*, **119**, 95.
[5] Hesse: *Ibid.*, **192**, 172.
[6] Schulze and Tollens: *Ibid.*, **271**, 49.

Influence of Inactive Substances on the Rotation of Glucose

Pribram[1] has determined the effect of addition of the following substances on the specific rotation of glucose, the end rotation reached in each case after long standing being finally measured .

1. *Ammonium Carbonate.*

Solutions which contained in 100 cc. 16.46 grams of anhydrous glucose and *p* grams of the salt gave .

$p =$	0	2	4	6	8	10
$[\alpha]^{20}_D =$	52 83	52 40	52 22	51.36	51 11	50 85°

There is, therefore, a slight decrease in the specific rotation of the glucose.

2 *Urea.*

The solutions contained in 100 cc , 15.797 grams of anhydrous glucose and *p* grams of urea .

$p =$	0	4	8	12	16
$[\alpha]^{20}_D =$	52.91	52.84	52.61	52.23	51 95°

There is also here a decrease in the specific rotation, but it is slight. According to Neumann Wender,[2] neither urea nor any other substance in urine has any effect on the rotation of glucose.

3. *Acetone.*

The solution contained in 100 cc., 15 68 grams of anhydrous glucose, *c* grams of acetone and water

$c =$	0	4	8	12	16	20	24	40	50
$[\alpha]^{20}_D =$	52.89	53 29	53 63	53 94	54 23	54 53	54 81	56.19	57 03°

The specific rotation of glucose increases in rather marked degree with increase in the acetone content of the solutions.

Alkalies and also lime bring about a gradual decrease in the rotation, and its final disappearance by decomposition and production of salts of saccharinic acid (left-rotating), glucinic acid, and humus-like bodies.

Derivatives of *d*-Glucose

Glucoseamine Hydrochloride, $CH_2.OH(CH.OH)_3.CH(NH_2)$

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[1] Sitzungsber d Wien Akad , **97**, II 375

[2] Ber d chem Ges , **24**, 2200

COH.HCl. Monosymmetric crystals. From lobster shells.

Water .... p 5.158, d_4^{20} 1.01865, t 20, $[\alpha]_D$ = +74.64° } [1]
" .... p 2.593, " 1.00853, t 20, " +70.61 }

Glucoseamine Hydrobromide, $C_6H_{13}NO_5.HBr$. Monosymmetric crystals.

Water .... p 22.555, d_4^{20} 1.1146, t = 20°, $[\alpha]_D$ = +59.37°
" .... p 12.505, " 1.0601, t = 20, " 59.63
" .... p 5.312, " 1.0237, t 20, " 60.23

The specific rotation increases therefore with the dilution according to the formula:

$$[\alpha]_D = 55.21 + 0.053q$$ [2]

Glucoseoxime, $C_6H_{12}O_5{:}NOH$. Colorless prisms; melting-point, 136° to 137°;[3] 135°.[4] Shows multirotation.

Water .... p 9.367, d 1.0295, t 20° } [5]
$[\alpha]_D$ after 15 minutes.. .... 5.5 }
" " 18 hours, constant................. 2.2 }

Glucose Trisulphuric Acid, $C_6H_9O_3(HSO_4)_3$.

Water. .. . . c 11, $[\alpha]_D$ +43.2° [6]

Glucose Tetrasulphuric Acid Chloride, $C_6H_7OCl(HSO_4)_4$. Square prisms.

Water .. .. c 4.4, $[\alpha]_D$ +71.8° [7]

Acetochlorhydrose (Glucose-monochlorhydrin-tetracetate), $C_6H_7(C_2H_3O)_4O_5Cl$.

$[\alpha]_D$ +117° [8]

Acetonitrose (Glucose tetracetate-mononitrate), $C_6H_7(C_2H_3O)_4.NO_2.O_5$. Crystals, melting-point, 145°.

$[\alpha]_D$ +159° [9]

Octacetyl Diglucose, $C_{12}H_{14}(C_2H_3O)_8O_{11}$.

I. Crystals; melting-point, 39° to 40°.

Water ..... t 16° to 17°, $[\alpha]_D$ +54.62° [10]

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[1] Wegscheider: Ber. d. chem. Ges., 19, 82.
[2] Tiemann, Landolt: *Ibid.*, 19, 155.
[3] Jacobi.
[4] Wohl: Ber. d. chem. Ges., 24, 995.
[5] Jacobi: *Ibid.*, 24, 997.
[6] Claesson: J. prakt. Chem., [2], 20, 26.
[7] Claesson.
[8] Colley: Compt. rend., 70, 401.
[9] Colley: *Ibid.*, 76, 436.
[10] Demole: Ber. d. chem. Ges., 12, 1936.

II. Cauliflower-like groups (from ether); melting-point, 128° to 133°.

Benzene .... $c = 2.415$, $[\alpha]_D = +22.50°$ [1]

Glucose Phenylhydrazone, $C_6H_{12}O_5(N_2H.C_6H_5)$.

Exists in two isomeric forms; the pure white crystals only, with melting-point 113 to 115, were investigated optically. They show strong multirotation.

p 9.181, d_4^{20} 1.0257, t 20°
$[\alpha]_D$ after 10 minutes .... 15.3°
" " 12 to 15 hours, constant. 46.9

The multirotation is not due to the fact that the substance had passed into the isomeric modification, because the crystals again obtained from the solution melt at 114°.[2]

Glucose Anilide, $C_6H_{11}O_5.HN.C_6H_5$. Sheaves of needles; melting-point about 147°.

Methyl alcohol (d_4^{20} 0.7907):
$p = 5.029$, $d_4^{20} = 0.8065$, t 20° to 23°, $[\alpha]_D$ 48.32°
$p = 3.326$, " $= 0.8055$, t 20° to 23°, " 49.15
Ethyl alcohol of 90 vol. per cent. (d_4^{20} 0.8294):
$p = 4.697$, $d_4^{20} = 0.8453$, t 20° to 23°, $[\alpha]_D$ 44.08°
$p = 3.269$, " $= 0.8407$, t 20° to 23°, " 44.15 } [3]

Glucose Paratoluide, $C_6H_{11}O_5.HN.(CH_3)C_6H_4 + {}^1/_2H_2O$. Crystals; melting-point, 106°.

Methyl alcohol (as above):
p 7.879, $d_4^{20} = 0.8243$, t 22° to 26°, $[\alpha]_D$ 43.88°
$p = 4.082$, " 0.8061, t 22° to 26°, " 42.55
$p = 2.613$, " $= 0.8007$, t 22° to 26°, " 38.23
Ethyl alcohol (as above):
p 6.658, d_4^{20} 0.8513, t 22° to 26°, $[\alpha]_D$ 38.80° } [4]

Glucose Ethylmercaptal, $C_6H_{12}O_5(SC_2H_5)_2$. Crystals.

Water.... p 4.878, d^{50} 1.002, t 50°, $[\alpha]_D$ 29.8° [5]

l-GLUCOSE.

From *l*-gluconic acid anhydride. Crystals; melting-point, 141° to 143°.

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[1] Herzfeld. Ann. Chem. (Liebig), **220**, 219.
[2] Jacobi: *Ibid.*, **272**, 171.
[3] Sorokin: J. prakt. Chem., [2], **37**, 295.
[4] Sorokin: *Ibid.*, [2], **37**, 308.
[5] Fischer: Ber. d. chem. Ges., **27**, 675.

Water .... p 4.114, d_4^{20} 1.016, t 20° [1]
$[\alpha]_D$ after 7 minutes 94.5
" " 7 hours, constant 51.4

MANNOSE (Seminose), $CH_2OH.(CH.OH)_4.CHO$.[2]

d-Mannose.

I. From mannitol by oxidation. Crystals.

Water ...... p about 10, d_4^{20} 1.0416, t 20°, $[\alpha]_D$ +12.96°[3]

II. From nut shells:

Water......... c about 10, t 20°, $[\alpha]_D$ +14.36°

The small difference is due to the amorphous nature of the latter product.[4]

d-Mannose Oxime, $C_6H_{12}O_5$:NOH. Crystals; melting-point 176°;[5] 176° to 184° (not constant).[6]

Exhibits multirotation. On account of the difficult solubility, a 5 per cent solution only could be investigated.

Water .. .. p 4.798, d 1.016, t 20° [7]
$[\alpha]_D$ after 10 minutes .. .. +7.5
" " 6 hours, constant .. . . . +3.2

l-Mannose. From *l*-mannonic acid anhydride. Sirup In aqueous solution rotates to the left.[8]

The phenylhydrazone, melting-point 195°, is right-rotating in hydrochloric acid solution; the phenylglucosazone, melting-point 205°, is strongly right-rotating in glacial acetic acid solution.[9]

RHAMNOHEXOSE, Methylhexose, $CH_3.(CHOH)_5.CHO$ $C_7H_{14}O_6$. From rhamnohexonic acid. Crystals; melting-point, 180° to 181°. Shows strong multirotation.

Water .... p 9.675, d_4^{20} 1.0347, t 20° [10]
After 1/2 hour.. ... ... $[\alpha]_D$ 82.9
After 12 hours, constant...... . .. . " 61.4

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[1] Fischer Ber d chem Ges, **23**, 2618
[2] Fischer, Hirschberger *Ibid.*, **22**, 1155
[3] Fischer, Hirschberger *Ibid.*, **22**, 365.
[4] Fischer and Hirschberger *Ibid.*, **22**, 3218
[5] Reiss, *Ibid.*, **22**, 611.
[6] Fischer and Hirschberger *Ibid.*, **22**, 1156.
[7] Jacobi, *Ibid.*, **24**, 698
[8] Fischer *Ibid.*, **23**, 373
[9] Fischer
[10] Fischer, Piloty. Ber d. chem Ges, **23**, 3102.

α-GLUCOHEPTOSE, $CH_2OH.(CH.OH)_5.CHO = C_7H_{14}O_7$. From α-glucoheptonic acid. Rhombic plates; melting-point, 180° to 190°. Shows weak birotation. For a solution made by gently warming with water, $c = 10$, $t = 20°$, $[\alpha]_D = -19.7°$ at once, and after fifteen minutes with greater dilution $[\alpha]_D = -25°$.[1]

β-Glucoheptose, not yet investigated.

d-MANNOHEPTOSE, $C_7H_{14}O_7$ (at 104°). Crystals; melting-point, 134° to 135° (not corr.). From *d*-mannoheptonic acid. Exhibits multirotation

Water .... $p = 10.807$, $d_4^{20} = 1.0397$, $t = 20°$ [2]
After 10 minutes . .. . $[\alpha]_D = +85.05$
After 24 hours, constant .. .. " $= +68.64$

l-Mannoheptose, from *l*-mannoheptonic acid, could not be obtained in a crystalline condition, but is characterized by its phenylhydrazone, melting at 196°, with complete decomposition.[3]

β-GALAHEPTOSE, $C_7H_{14}O_7$. Melting-point, 190° to 194°. Shows multirotation.

Water...... $p = 9.2$, 10 minutes after solution $[\alpha]_D^{20} = -22.5°$
After 24 hours $[\alpha]_D^{20} = -54.4°$ [4]

RHAMNOHEPTOSE, $C_8H_{16}O_7$ From rhamnoheptonic acid.

Water .... .. $c = 9.40$, $t = 20°$, $[\alpha]_D = +8.4°$ (about)

α-GLUCOOCTOSE, $C_8H_{16}O_8 + 2H_2O$. From α-glucooctonic acid. Needles; melting-point, 93° (uncorr.) Shows multirotation.

Water.. ...... $p = 6.496$, $d = 1.0213$, $t = 20°$ [5]

		Hydrated	Anhydrous
After a short time..... .	$[\alpha]_D =$	$-61.5°$	$-70.8°$
After 6 hours, constant .	" $=$	-43.9	-50.5

d-MANNOOCTOSE, $C_8H_{16}O_8$. From *d*-mannooctonic acid. Colorless sirup.

$[\alpha]_D^{20}$ (approx.) $= -3.3°$ [6]

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[1] Fischer Ann. Chem (Liebig), **270**, 64

[2] Fischer, Passmore Ber d chem Ges, **23**, 2228

[3] Smith Ann Chem (Liebig), **272**, 183.

[4] Fischer *Ibid.*, **288**, 155

[5] Fischer *Ibid*, **270**, 64

[6] Fischer, Passmore Ber d chem Ges, **23**, 2234

GALAOCTOSE, $C_8H_{16}O_8 + H_2O$. From galaoctonic acid lactone. Thin plates, melting-point, 109° to 111°.

$$[\alpha]_D > -40°$$ [1]

d-MANNONONOSE, $C_9H_{18}O_9$. From *d*-mannononic acid. Crystals; melting-point about 130°.

$$[\alpha]^{20}_D \text{ (approx.) } = +50.0°$$ [2]

17. Oxyketones. Ketoses

d-FRUCTOSE, levulose, fruit-sugar, $CH_2OH.(CH.OH)_3.CO.CH_2OH = C_6H_{12}O_6$. This body shows left rotation in aqueous solution, which, as first shown by Dubrunfaut,[3] decreases rapidly with elevation of temperature. Besides this, the freshly dissolved fructose shows multirotation (§72). The numerical data given below hold for the constant end rotation.

On the production of pure levulose from inulin, see Wohl.[4]

Earlier investigations by Herzfeld,[5] Winter,[6] Herzfeld and Winter[7] gave specific rotations which, for example, for $p = 20°$ and $t = 20°$, varied between $[\alpha]_D = -70.59°$ and $-71.47°$.

The following observers found a much higher value.

1. Hönig and Jesser.[8] They give the formulas

a. For the influence of temperature:

$$\text{For } p = 9, \quad [\alpha]^t_D = -103.92 + 0.671\,t, \quad \text{for } t = 13° \text{ to } 40°$$
$$\text{" } p = 23.5, \quad \text{" } = -107.65 + 0.692\,t, \quad \text{" } t = 9° \text{ to } 45°,$$

b. For the effect of the percentage amount of water q in the solution,

$$[\alpha]^{20}_D = -113.96 + 0.258\,q, \quad \text{for } q = 60 \text{ to } 95 \text{ per cent.},$$

from which follows

For $100 - q = p =$	5	10	20	30	40
$[\alpha]^{20}_D =$	−89.42	−90.72	−93.30	−95.88	−98.47°

According to Honig and Jesser, the lower values of Herzfeld depend on this, that in the conversion of inulin into sugar dextrines are always formed which, by the method of purification with ether-alcohol employed by the latter, cannot be completely removed.

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[1] Fischer. Ann. Chem. (Liebig), **288**, 150.

[2] Fischer, Passmore.

[3] Compt. rend., **42**, 901.

[4] Ber. d. chem. Ges., **23**, 2107.

[5] Ann. Chem. (Liebig), **244**, 287.

[6] *Ibid.*, **244**, 300.

[7] Ber. d. chem. Ges., **19**, 393.

[8] Ztschr. für Rübenzucker-Ind., (1888), p. 1028.

2. Jungfleisch and Grimbert[1] combine the following determinations, made for different concentrations and temperatures:

$c = 9.75$		$c = 48.75$		$t = 17°$	
t	$[\alpha]_D$.	t	$[\alpha]_D$	c	$[\alpha]_D$.
7°	−97.31	0°	−105.76	9.75	91.55
17	−91.55	7	−102.20	19.5	−92.72
20	−89.90	16	−97.62	39.0	95.30
		28	−90.39	48.75	97.07
		40	−82.53		

under the general formula.

$$[\alpha]^t_D = -[101.38 - 0.56\,t + 0.108\,(t - 10)].$$

Ost[2] investigated fifteen solutions, the strength of which varied between 1 and 30 per cent. of levulose, at 20°, and calculated this formula.

$$[\alpha]^{20}_D = -(91.90 + 0.111\,p)$$

4. Parcus and Tollens[3] found

for $p = 10$, $t = 20°$, $[\alpha]_D = -92$ to $92.5°$

5. Wohl found[4]

for $p = 10.17$ or $c = 10.57$, $t = 20°$, $[\alpha]_D = -91.8°$

According to the above five observers, the specific rotation of a 10 per cent. solution at the temperature of observation varies between $[\alpha]_D = -90.2°$ and $93°$.

In alcoholic solution, levulose has about two-thirds the rotation shown in water.

With reference to the multirotation, or decrease in the rotation of freshly prepared solutions, we have the following observations:

1. Parcus and Tollens:[5]

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[1] Compt. rend., **107**, 390.
[2] Ber. d. chem. Ges., **24**, 1636.
[3] Ann. Chem. (Liebig), **257**, 160.
[4] Ber. d. chem. Ges., **23**, 2090.
[5] Ann. Chem. (Liebig), **257**, 6.

$c = 10$, $t = 20°$, First rotation after 6 min $[\alpha]_D = -104.0°$
End rotation " 25 " " $= -92.3$
and 1 hour $[\alpha]_D = -92.1$

2. Schulze and Tollens [1]

$c = 10$, $t = 20°$, First rotation after 15 min. $[\alpha]_D = -92.3°$
End rotation " 20 hours " $= -90.9$

In 0.1 per cent. ammonia the constant end rotation is reached in five minutes.

3 Jungfleisch and Grimbert[2] give, among others, the following observations

$c = 1.779$, $t = 8°$			$c = 9.75$, $t = 7°$		
After 10 min	$[\alpha]_D =$	$-106.02°$	After 35 min.	$[\alpha]_D =$	$-97.33°$
" 20 "	" $=$	-99.32	" 55 "	" $=$	-96.11
" 45 "	" $=$	-93.83	" 75 "	" $=$	-95.11
" 90 "	" $=$	-92.00	" 105 "	" $=$	-94.77

If the levulose solution in water is heated, a further gradual reduction takes place according to Jungfleisch and Grimbert, and to avoid this, the temperature should not go above 40°. But Ost[3] did not observe this decrease.

According to their strength, acids affect the specific rotation of levulose in different ways (Dubrunfaut, Jungfleisch and Grimbert, Ost)

Levulose anilide is characterized by a very high rotation Sorokin[4] found

In ethyl alcohol $p = 0.712$............ $[\alpha]_D = -215.7°$
" " " $p = 2.016$ ...... " $= -185.5$
In methyl alcohol $p = 1.436$........... " $= -181.5$

18. Invert Sugar

The rotating power of the invert sugar solutions obtained by the action of acids on cane-sugar solutions has been investigated mainly by Gubbe,[5] Ost,[6] Wohl,[7] and others. As Gubbe, and later Ost found, the inversion is most conveniently accomplished by heating 100 parts of cane-sugar with 1 part of oxalic acid, in aqueous solution, for several hours to 50° or 60°. No modification of the rotation of the invert sugar takes place here as is the case on heating with hydrochloric or sulphuric acid.

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[1] Ann. Chem. (Liebig), **271**, 53.

[2] Compt rend, **107**, 390.

[3] Ber. d. chem Ges, **24**, 1643

[4] J prakt Chem, [2], **37**, 195

[5] Ber d chem Ges, **18**, 2207

[6] *Ibid.*, **24**, 1640

[7] *Ibid.*, **23**, 2087

The rotation of this sugar mixture is subject to many changes, and the following conditions have especial influence.

a. Concentration.—From careful experiments, Gubbe deduces the following formulas, based on a temperature of 20° :

$$\text{(I)} \qquad [\alpha]_D^{20} = -19.447 - 0.06068\,p + 0.000221\,p^2$$
$$\text{(II)} \qquad \text{“} \quad = -23.305 - 0.01649\,q + 0.000221\,q^2,$$

holding for $p = 9$ to 68, or $q = 32$ to 91 ;

$$\text{(III)} \qquad [\alpha]_D^{20} = -19.657 - 0.0361\,c,$$

holding for c up to 35.

Ost gives the expression

$$[\alpha]_D^{20} = -19.82 - 0.04\,p,$$

holding for $p = 2$ to 30.

b. Temperature.—This formula was given by Tuchschmidt,[1] for $c = 17.21$ and $t = 5$ to 35,

$$[\alpha]_D^t = -27.9 + 0.32\,t$$

Lippmann found nearly the same in a series of experiments extending to $t = 80°$.[2]

More accurate formulas deduced by Gubbe from his experiments are these

$$\text{(IV) For } t = 0° \text{ to } 30° \quad [\alpha]_D^t = [\alpha]_D^{20} + 0.3041\,(t-20) + 0.00165\,(t-20)^2$$
$$\text{(V)} \quad \text{“} \quad t = 20° \text{ “ } 100° \quad \text{“} = \text{“} + 0.3246\,(t-20) - 0.00021\,(t-20)^2$$

If we calculate the values for different percentage strengths and temperatures of invert sugar solutions according to Gubbe's formulas, I and IV, we obtain this table

	$c = 5$	$c = 10$	$c = 15$	$c = 20$	$c = 25$	$c = 30$	δ for $t = 5°$
$t = 5°$	− 24.03	− 24.21	− 24.39	− 24.58	− 24.75	− 24.93	1.31
10	− 22.72	− 22.90	− 23.08	− 23.26	− 23.44	− 23.62	1.40
15	− 21.32	− 21.50	− 21.68	− 21.86	− 22.04	− 22.22	1.48
20	− 19.84	− 20.02	− 20.20	− 20.38	− 20.56	− 20.74	1.56
25	− 18.28	− 18.46	− 18.64	− 18.82	− 19.00	− 19.18	1.65
30	− 16.63	− 16.81	− 16.99	− 17.17	− 17.35	− 17.53	
δ for $c = 5$	0.18	0.18	0.18	0.18	0.18		

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[1] J prakt Chem, [2], 2, 235

[2] Ztschr fur Rübenzucker-Ind., 4, 303.

As the rotation of invert sugar solutions decreases with temperature elevation, it must follow that it becomes 0 at some definite temperature and changes to right rotation at a still higher heat. This temperature of inactivity is 87.2° according to Tuchschmidt, and 87.8° according to Lippmann.

For solutions inverted with oxalic acid, Gubbe found these temperatures.

$$79.39^\circ\ (c = 10), \quad 80.43^\circ\ (c = 20), \quad 81.47^\circ\ (c = 30)$$

The decrease and final change in direction of rotation is explained by the fact that the rotating power of levulose diminishes rapidly with increasing temperature, while that of dextrose is but slightly changed.

c. Presence of Acids.—That the specific rotation of invert sugar solutions made from cane-sugar suffers a change by reason of different amounts of acids employed was shown first by Dubrunfaut,[1] and later by Gubbe.[2] According to the experiments of the latter, hydrochloric and sulphuric acids produce an increase in the specific rotation, which, for solutions containing 10 parts of invert sugar in 100 parts of water and s parts of acid, may be expressed by the following formulas

Sulphuric acid . . $[\alpha]_D^{20} = -(19.983 + 0.1698\,s)$ holding for $s = 0.1$ to 5
Hydrochloric acid " $= -(19.995 + 0.3262\,s)$ " " $s = 0.1$ to 3

If, however, cane-sugar is inverted with different amounts of oxalic acid (0.1 to 4.3 parts for 10 parts of invert sugar and 100 parts of water), the specific rotation remains constant.

If an invert sugar solution is warmed with hydrochloric acid and then diluted, the liquid does not assume the proper end rotation corresponding to the dilution until after about twenty-four hours.[3]

d. Temperature of Inversion.—Invert sugar solutions made by action of mineral acids on cane-sugar solutions, with application of heat, suffer a decrease in the rotation if the heating is increased or long-continued.

There are no accurate experiments on this, but only occasional statements. According to Herzfeld,[1] if a solution containing 13.024 grams of cane-sugar in 50 cc. of water is warmed with 5 cc. of 38 per cent. hydrochloric acid to 69°, the inversion is complete in seven minutes, and in fifteen minutes, a decrease in the rotation has already begun. Under the same conditions, but employing 75 cc of water, the maximum rotation is again reached in seven minutes and the decrease begins in twenty minutes Wohl[2] also found that when invert sugar solutions are warmed with hydrochloric acid for some time, the left rotation as well as the copper oxide reducing-power decreases more and more, because dextrine-like products are formed from the levulose.

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[1] Compt rend, **23**, 38
[2] Ber d chem Ges, **18**, 2210
[3] Gubbe, *Ibid*, **18**, 2211, Wohl *Ibid*, **23**, 2087

In general, the velocity of inversion increases rapidly with the temperature, and for all acids In addition, when strong acids are used, it is increased by the presence of neutral salts of the same acids, which action, however, diminishes with elevation of temperature.[3]

c. Formation of Dehydration Products—If acid-free invert sugar solutions are evaporated *in vacuo* to a sirup, dehydration compounds (right-rotating levulosan) are formed, and on resolution a much weaker left rotation, or even a right rotation, is found On standing several hours in the cold or after heating a short time to 67° to 70° with addition of hydrochloric acid, the normal rotation returns [4]

b. Behavior of Inactive Bodies.—Alcohol greatly decreases the left rotation of invert sugar, and on warming, right rotation may appear.[5] According to Landolt,[6] a solution of 20 grams of invert sugar in 15 cc. of water and diluted with absolute alcohol to 100 cc. is inactive at 38°, and rotates above this temperature to the right, and below it to the left. According to Horsin-Déon, anhydrous invert sugar dissolved in absolute alcohol shows no rotation, but becomes left-rotating on addition of water.

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[1] Ztschr fur Rubenzucker-Ind (1888), p 707

[2] Ber. d chem Ges, **23**, 2096

[3] Spohr J prakt Chem, [2], **32**, 32

[4] Degener Ztschr fur Rübenzucker-Ind (1886), p. 344; Herzfeld *Ibid* (1887), p 908

[5] Jodin Compt rend, **58**, 613

[6] Ber d chem Ges, **13**, 2335

Lime produces a decrease in the left rotation.[1]

Basic lead acetate added in increasing amounts to an invert sugar solution decreases the left rotation, and converts it into increasing right rotation.[2]

On employing a basic lead acetate solution of 1.222 sp. gr., Bittmann[3] found these deviations in the Ventzke saccharimeter.

Invert sugar solution cc	Water cc	Basic lead acetate cc.	Ventzke degrees
50	50	..	— 2.3°
50	40	10	— 1.0
50	30	20	+ 3.7
50	10	40	+ 7.5
10	40		— 2.2°
10	30	10	+ 1.5
10	.	40	+ 6.4
5	5	40	+ 7.6

Invert sugar solution cc	Alcohol cc	Basic lead acetate cc	Ventzke degrees
10	40		— 0.4°
10	30	10	+ 4.0
10	20	20	+ 6.9
5	45		— 0.4°
5	35	10	+ 8.6

Composition of Invert Sugar—For a long time it has been assumed that invert sugar is a mixture of equal parts of dextrose and levulose, but it is only recently that the correctness of this assumption has been shown by Hönig[4] and Jesser, which they did by proving that the arithmetical mean of the specific rotations of the two components coincides with the specific rotation of invert-sugar. This proof was never successful before, because sufficient knowledge of the numerical data in question was lacking. These data are given by the following formulas:

---

[1] Jodin *Loc. cit*

[2] C. Haughton Gill: J Chem Soc, 24, 91.

[3] Ztschr für Rübenzucker-Ind., (1880), p 876

[4] *Ibid.*, (1888), p 1037.

Dextrose .... $[\alpha]_D^{20} = + 52.50 + 0.0188\ p + 0.000517\ p^2$ [1]
Levulose .... " $= - 88.13 - 0.2583\ p$ [2]
Invert sugar .... " $= - 19.447 - 0.06068\ p + 0.000221\ p^2$ [3]

If now the specific rotations of these sugars for different strengths, p, be calculated, we have from the above formulas:

p	Dextrose	Levulose	Arithmetical mean	Invert-sugar	Difference
20	+ 53.08	− 93.30	− 20.11	− 20.57	+ 0.46
25	+ 53.29	− 94.59	− 20.65	− 20.83	+ 0.18
30	+ 53.53	− 95.88	− 21.18	− 21.07	− 0.11
35	+ 53.79	− 97.17	− 21.69	− 21.30	− 0.39

The same calculation has been carried out by Ost [4]

The agreement with observation confirms the above assumption fully and an earlier suggestion of Winter[5] that invert sugar may be made up of 4 parts of levulose and 3 parts of dextrose is evidently in error.

19. Disaccharides (Saccharoses, Bioses)

CANE-SUGAR, $C_{12}H_{22}O_{11}$. Right-rotating.

For the relation of the specific rotation of the sugar in aqueous solution to

1. The percentage amount p of sugar,
2. The percentage amount q of water,
3. The concentration c, or grams of sugar in 100 cc., the following formulas have been given, based on accurate observations

I. By Tollens.[6] Calculated from 19 solutions.

1. Specific gravity of the solutions at 17.5°, referred to water at 4°. Rotation at 20°:

$$a \begin{cases} p = 4 \text{ to } 18, & [\alpha]_D = 66.810 - 0.015553\ p - 0.0_4 52462\ p^2 \ {}^{7} \\ q = 82 \text{ to } 96, & \text{''} \ = 64.730 + 0.026045\ q - 0.0_4 52462\ q^2 \end{cases}$$

$$b. \begin{cases} p = 18 \text{ to } 69, & \text{''} \ = 66.386 + 0.015035\ p - 0.0_3 3986\ p^2 \\ q = 31 \text{ to } 82, & \text{''} \ = 63.904 + 0.064686\ q - 0.0_3 3986\ q^2 \end{cases}$$

---

[1] Tollens.

[2] Hönig and Jesser

[3] Gubbe

[4] Ber d chem Ges, **24**, 1640

[5] Ann Chem. (Liebig), **244**, 295 and 329

[6] Ber d chem Ges, **10**, 1403

[7] $0.0_4 52462 = 0.000052462$, etc

Later, Tollens[1] found that the formulas *b* satisfy dilute solutions also, down to $p = 1$ even.

2. Specific gravity of solutions at 17.5° referred to water at 17.5° Rotations at 20°.

From the same experiments as under 1 there follows for p.

$$a'.\ p = 4 \text{ to } 18, \quad [\alpha]_D = 66.727 - 0.015534\,p - 0.0_4 52396\,p^2$$
$$b'.\ p = 18 \text{ to } 69, \quad \text{"} \quad = 66.303 - 0.015016\,p - 0.0_8 3981\,p^2$$

By another method of calculation, Thomsen[2] obtained from the observations of Tollens these expressions in place of those given under *b* above,

$$b''.\ \begin{cases} p = 18 \text{ to } 69, & [\alpha]_D = 66.577 + 0.007466\,p - 0.0_8 31339\,p^2 \\ q = 31 \text{ to } 82, & \text{"} \quad = 64.190 + 0.055212\,q - 0.0_8 31339\,q^2, \end{cases}$$

which agree well with the Schmitz formulas given below under II., 1.

II. Schmitz[3] gives these formulas deduced from eight solutions (see §54, p. 195)

1. Specific gravity of the solutions at 20° referred to water at 4°. Rotations at 20°.

$$p = 5 \text{ to } 65, \quad [\alpha]_D = 66.510 + 0.004508\,p - 0.0_3 28052\,p^2$$
$$q = 35 \text{ to } 95, \quad \text{"} \quad = 64.156 + 0.051596\,q - 0.0_3 28052\,q^2$$

2. For the concentration at 20° Schmitz gives these formulas

$$c = 10 \text{ to } 86, \quad [\alpha]_D = 66.453 + 0.001236\,c - 0.0_3 11704\,c^2$$
$$c = 2.5 \text{ to } 28, \quad \text{"} \quad = 66.639 - 0.020820\,c + 0.0_3 34603\,c^2$$
$$c = 2.5 \text{ to } 28, \quad \text{"} \quad = 66.541 - 0.008415\,c$$

Landolt[4] has calculated these approximate expressions from the observations of Tollens amd Schmitz, showing the relation of the specific rotation and concentration of solutions:

$$c = 4.5 \text{ to } 27.7, \quad [\alpha]^{20}_D = 66.67 - 0.0095\,c \text{ (true cc.)}$$
$$c = 4.5 \text{ to } 27.7, \quad [\alpha]^{17.5}_D = 66.82 - 0.0096\,c \text{ (Mohr's cc.)}$$

III. The latest experiments have been carried out by Nasini and Villavecchia.[5] These formulas follow from twelve series of observations with different sugars

$$p = 3 \text{ to } 65, \quad [\alpha]^{20}_D = 66.438 + 0.010312\,p - 0.0_3 35449\,p^2$$
$$q = 35 \text{ to } 97, \quad \text{"} \quad = 63.924 + 0.060586\,q - 0.0_3 35449\,q^2$$

---

[1] Ber. d. chem Ges., **17**, 1751

[2] *Ibid*, **14**, 1652

[3] *Ibid.*, **10**, 1414.

[4] *Ibid*, **21**, 196.

[5] Public. de lab chim. centr delle gabelle, Roma (1891), p. 47.

If we combine now the results which the different formulas give for a number of different percentage amounts of sugar, we find these variations:

	Formula $p =$	10	20	30.	40.	50
I*a*	Tollens	66.65	66 48	66 30	66 10	65 90
I*b*	Tollens	66 50	66 53	66.48	66 35	66.14
I*b''*.	Tollens-Thomsen	66 62	66 60	66.52	66 37	66 17
II.	Schmitz	66.53	66.49	66 39	66 24	66 03
III	Nasini and Villavecchia	66 51	66.50	66.43	66 28	66.07

It is seen that the values given by the last two formulas furnish the closest agreement.

With reference to the specific rotation of cane-sugar in very dilute solutions, see the observations given already in §55.

For the rotation of different rays of light by cane-sugar, see "Rotation Dispersion," §45.

Influence of temperature. This was formerly held by Mitscherlich,[1] Hesse,[2] also Tuchschmidt[3] to be extremely small. Andrews[4] was the first to show that the specific rotation of sugar decreases with elevation of temperature and to the extent of 0 0114 for 1° C. According to new experiments which Schönrock[5] has carried out, using ten sugar solutions, the temperature coefficient lies between 0 0132 and 0.0151 This formula may be used to calculate the specific rotation of solutions of about 24 per cent. strength, for a temperature different from 20°, between the limits, 12° and 25°.

$$[\alpha]^t_D = [\alpha]^{20}_D - 0\ 0144\ (t - 20)$$

Recently Wiley[6] has reinvestigated the subject with extreme care and has found a value lower than those given above. The coefficient as given by him is 0.00994 as the mean change in the specific rotation for each degree centigrade.

In the paper by Andrews, the value is given in one place as

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[1] Ber d Berl Akad , (1842), p. 150

[2] Ann Chem (Liebig), **176**, 97

[3] J prakt Chem , [2], **2**, 244

[4] Technology Quarterly, May (1889), p 367 . Chem. Centrbl , (1890), I, p 20.

[5] Ber. der phys.-techn Reichsanstalt von 1896 , Ztschr für Instrum., **17**, 180.

[6] J Am Chem Soc , **21**, 568 (1899).

0.000114. But the context shows that this is a typographical error for 0.0114.

On the specific rotation of cane-sugar in mixtures of water with acetone, methyl alcohol, and ethyl alcohol, see §59. According to Seyffart,[1] sugar retains the same specific rotation when dissolved to the extent of 5 to 40 grams in 100 cc. of alcohol of 9° to 90°.[2]

The changes shown in the specific rotation of cane-sugar in presence of alkalies and salts have been explained already in §70.

MILK-SUGAR Lactose, Lactobiose. Anhydrous, $C_{12}H_{22}O_{11}$, hydrated, $C_{12}H_{22}O_{10} + H_2O$.

As already shown in the chapter on multirotation, §72, this sugar is found in three modifications, of which α and γ in aqueous solution pass slowly into β at the ordinary temperature, but rapidly on warming. The α-form exhibits greater rotation (birotation), and the γ-form less rotation (half rotation) (see §71)

				Anhydride	Hydrate
1	α-Modif	ordinary milk-sugar .	$[\alpha]_D$	+ 88°	+ 84°
2	β- "	stable form.....	"	+ 55 30	+ 52 53
3	γ- "	second labile form.	"	+ 36 2	+ 34 4

Ordinary Milk-Sugar.—The beginning rotation of this cannot be accurately determined, because of rapid change into the β-form, and is always found too small Schmöger[3] found $[\alpha]_D = + 84°$ (for the hydrate), and Parcus and Tollens[4] + 83°.

The following series of experiments by Parcus and Tollens gives a picture of the change into the stable β-form which follows in milk-sugar solutions at the temperature of 20°, the time being counted from the moment of adding water to the finely powdered substance

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[1] Ztschr für Rübenzucker-Ind (1879), III, p 130

[2] Tralles

[3] Ber. d chem. Ges., 13, 1918.

[4] Ann. Chem. (Liebig), 257, 170.

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$t = 20°$ $c = 4\ 841$		$t = 20°$ $c = 7\ 064$	
Time	$[\alpha]_D$	Time	$[\alpha]_D$
8 min	82 91°		
10 "	82 56		
15 "	81 12		
20 "	79 69	25 min.	78.86°
30 "	76.48	30 "	77.14
45 "	73.26	40 "	74.94
1 hour	70.04		
1½ hours	65.76	1½ hours	68.57
2 "	62 17	2 "	61.70
2½ "	58 97		
3 "	57 54	3½ "	55 84
4½ "	54 32		
5 "	53 60	5 "	54 25
6 "	53 43		
7 "	53.25	7 "	52 90
24 "	52 53	24 "	52 53

As opposed to the earlier statements of Hesse,[1] Schmoger[2] shows that the rotating power of milk-sugar for $c = 2.372$ to 41.536 is independent of the concentration He finds from the mean of 70 polarizations the constant rotation at 20°, for

$$C_{12}H_{22}O_{11} + H_2O \ \ldots\ldots\ldots \ [\alpha]_D = +\ 52\ 53°$$

Exactly the same value is found by Deniges and Bonvans.[3] However, according to experiments of Schmoger, the temperature influences the rotating power which sinks as the solution becomes warm This effect is greater at 20° than at higher temperatures. In the neighborhood of $t = 20°$, $[\alpha]_D$ changes about 0 070° for one degree of temperature as shown by the following table

p	d_4^{20}.	$[\alpha]_D$ at								
		9°	10°	14°	20°	21°	32°	33°	35°	37°
8 307	1 0301			52 76°	52 36°		51.60°			
15.950	1.0661		53.50°		52.56					51 40°
16.664	1.0642	53 46°				52 36°			51.48°	
24.785	1 0992				52.56			51 59°		

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[1] Ann Chem (Liebig), 176, 98

[2] Ber d chem Ges, 13, 1922

[3] J pharm. chim, [5], 17, 363. Chem Centrbl (1888), p 603

If the rotation, α_t, of a milk-sugar solution has been found at the temperature t, it may be reduced to the value at 20° by this formula:

$$\alpha_{20} = \alpha_t + \frac{1020 - t}{1000}.$$

By the action of dilute acids, milk-sugar is inverted and glucose and galactose are formed, which may be shown by polarization. If, for example, $c = 11.9734$ and $t = 20°$, there may be calculated from the rotation of glucose, $[\alpha]_D = 52.84°$, and of galactose, $[\alpha]_D = 79.73°$, that of the inverted milk-sugar as $\frac{52.84 + 79.73}{2} = 66.29°$. Rindell[1] found $[\alpha]_D = 67.57$ for this rotation, and showed that it is influenced by the temperature according to the following formula

$$[\alpha]_D = 70.608° - 0.152\,t.$$

Alkalies diminish the rotating power of milk-sugar.

1 mol cryst. milk-sugar + 1 mol. Na_2O

$t = 20°$, $c = 3$, $[\alpha]_D$ at once. ...... $= +45.5°$ ⎫[2]
$t = 20°$, $c = 3$, " after 24 hours. $+12.57$ ⎭

Half-Rotating Milk-Sugar (γ-form) This is produced as already explained in §72 The beginning rotation is found too large because of the rapid conversion into the more strongly rotating β-form Schmöger[3] obtained for

$c = 7.07$, $[\alpha]_D = +34.4$, $c = 7.72$, $[\alpha]_D = +36.2°$

The conversion of α- and also γ-milk-sugar into the constant β-form is hastened by addition of 0.1 per cent. ammonia[4]

Milk-Sugar Octoacetate, $C_{12}H_{14}O_{11}(C_2H_3O)_8$. This is left-rotating and exhibits neither birotation nor half-rotation.

Chloroform .... $p =$ about 10, $[\alpha]_D = -3.5°$[5]

MALTOSE, Maltobiose, Malt Sugar, Ptyalose, $C_{12}H_{22}O_{11} + H_2O$ Crystallizes in fine needles with 1 molecule of water of crystallization, which is lost at 100°.

The earlier statements on the rotation of maltose gave values between $[\alpha]_D = +139°$ and 150°. The first reliable observations were made by Meissl.[1] He found that maltose, li lactose, shows half-rotation.

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[1] Ztschr. für Rübenzucker-Ind, **4**, 163

[2] Hesse. Ann. Chem. (Liebig), **176**, 101.

[3] Ber. d. chem. Ges, **13**, 1918.

[4] Schulze and Tollens · Ann. Chem (Liebig), **271**, 49

[5] Schmöger Ber. d. chem. Ges, **25**, 1452

c.	$[\alpha]_D$ after						
	5 min.	1 hour.	4 hours	7 hours.	8 hours.	24 hours.	4 da
15.61	122.6	126.2	132.0	137.0	137.2	138.3	138.
18.94	122.5	127.4	133.0	137.6	138.2	138.2	138.
19.4	122.0	127.0	135.0	138.0	138.3	138.3	138.

Parcus and Tollens[2] also investigated the half-rotation in t different solutions, and found :

Preparation 1		Preparation 2			
$l = 20^0$ $c = 10.040$ for hydrate $c = 9.537$ for anhydr		$l = 20^0$. $c = 9.679$ for hydrate $c = 9.195$ for anhydr.		l 20^0 c 10.320 for hydrat c 9.804 for anhyd	
Time	$[\alpha]_D$ for anhydride.	Time.	$[\alpha]_D$ for anhydride.	Time.	$[\alpha]_D$ f anhydri
8 min.	119.36°	12 min.	120.97°	6 min.	118.75°
10 "	120.27	14 "	121.16	8 "	119.46
15 "	121.01	16 "	122.29	10 "	120.34
20 "	121.72	20 "	123.23	12 "	120.69
30 "	123.35	25 "	124.55	15 "	121.22
45 "	125.17	30 "	125.68	20 "	122.28
1 hour	128.07	40 "	127.56	30 "	124.04
1½ hours	130.97	50 "	129.44	50 "	127.04
2 "	132.97	1 hour	130.57	1 hour	128.81
2½ "	134.05	1¼ hours	132.63	1½ hours	131.45
3 "	134.96	1¾ "	134.71	2 "	133.22
5 "	136.52	2 "	135.27	3 "	135.16
7 "	136.72	2¼ "	135.65	4½ "	136.40
9 "	136.96 const	3¾ "	136.40	6 "	136.75 co
		5 "	136.87 const.		

The constant end rotation, as with milk-sugar, is m quickly reached by heating the solution or by adding amn nia to it.[3]

---

[1] J prakt. Chem., **21**, 284 and **25**, 114.

[2] Ann. Chem. (Liebig), **257**, 172.

[3] Schulze and Tollens : *Ibid.*, **271**, 53.

The constant end rotation is dependent on the temperature and concentration, as shown by observations of Meissl,[1] which may be expressed by this formula

$$[\alpha]_D = 140\ 375 - 0.01837\,p - 0\ 095\,t$$

From this we have the following agreement between observation and calculation:

p	d at 17 5°	$[\alpha]_D$ at							
		15°		17 5°.		25°.		35°	
		Found	Calc	Found.	Calc.	Found	Calc	Found	Calc
4 95	1 01961	138.67	138 86	138.46	138 62	137.97	137.91	137 08	136 96
9 70	1.03928	138 79	138.77	138.54	138.53	137 84	137.82	136.95	136.87
18.65	1.07777	138 56	138 61	138.33	138.37	137.57	137 66	136.75	136 71
18.67	1 07779	138 68	138.61	138.40	138.37	137.68	137 66	136.79	136 71
19.68	1.08281	138 70	138 59	138.30	138 35	137 59	137.64	136.66	136 69
19 91	1 08309	138 50	138 58	138 39	138.34	137.55	137 63	136 61	136 68
33 86	1 14873	138 35	138 33	138 12	138 09	137 33	137 38	136 38	136 43
34.72	1.15361	138 26	138 31	138 00	138 07	137 29	137 36	136.37	136 41
34 95	1.15500	138 34	138 31	138 11	138.07	137.40	137 36	136.48	136 41

Herzfeld[2] gives:

Water.. . .. $t = 20°$, p 11 29, d_4^{20} 1 044°, $[\alpha]_D$ + 138 29°

(From Meissl's formula there is calculated 138 27)

Ost[3] finds

Water . . . c 2 to 21, $t = 20°$, $[\alpha]_D = +\ 137\ 04°$

Brown, Morris and Millar[4] also obtain values which closely agree with those of Meissl.

Octacetyl Maltose, $C_{12}H_{11}O_{11}(C_2H_3O)_8$. Crystals, melting-point, 150° to 155°

Benzene .... c 1.9956, $[\alpha]_D$ — 81.18°[5]
Benzene .... p - 2 " — 75.7 }[6]
Alcohol .... p = 2 " = 60.0 }
Benzene........ p - 2 " — 76.54 }[7]
Chloroform ..... p — 2 " — 61.01 }
Alcohol .... p — 1 " — 60.02 }

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[1] J. prakt. Chem [2], **25**, 114.

[2] Ztschr für Rübenzucker-Ind., (1895), p. 236.

[3] Chem Ztg., **19**, 1727

[4] J Chem Soc, **71**, 72.

[5] Herzfeld, Ann. Chem (Liebig), **220**, 218.

[6] Herzfeld: Ztschr. für Rübenzucker-Ind, (1895), p. 235.

[7] Herzfeld Ber d chem. Ges, **28**, 441.

ISOMALTOSE Gallisin, $C_{12}H_{22}O_{11}$. This is formed in the yeas fermentation of grape-sugar,[1] or in the treatment of this suga with hydrochloric acid.[2]

The specific rotation in aqueous solution increases approximately in proportion to the amount of solvent employed:

Water....... $t = 20°$, $c = 54.58$, $[\alpha]_D = +77.32°$ }[3]
$c = 27.29$, " $+80.10$
$c = 10.60$, " $+82.76$

Lintner and Düll[4] give for a preparation of isomaltose fro starch, but which probably was not pure, $[\alpha]_D = 140°$ in 1 per cent. solution.

TREHALOSE, Mycose, $C_{12}H_{22}O_{11} + 2H_2O$. Rhombic crystals melting-point, 210°.

Water.... $c = 8.4$ to 14.8 $t = 15°$
$[\alpha]_D = +199°$ (= 220° for anhydrous subst.)[5]
Water.... $c = 10.03$, $[\alpha]_D = +173.2°$[6]

MELIBIOSE, Raffinoboise, $C_{12}H_{22}O_{11}$. Amorphous powder.

Water............ $c = 3.957$, $t = 17°$, $[\alpha]_D = +126.7°$
Water............ $c = 3.973$, $t = 17$, " $+127.9$

These are only approximate values, as we have no guarante of the purity of the amorphous sugar.[7]

Water.......... $t = 17.5°$, $[\alpha]_D = 137.32°$[8]

Octacetyl Melibiose, $C_{12}H_{14}O_{11}(C_2H_3O)_8$.

$^2/_3$ Alcohol + $^1/_3$ chloroform.... $c = 1.6516$, $t = 18°$, $[\alpha]_D = +91.2°$

CYCLAMOSE, $C_{12}H_{22}O_{11}$. From the roots of *Cyclamen eu paeum*. The specific rotation is not affected by the temperature, and is

$$[\alpha]_D = -15.15°.$$

On heating with dilute hydrochloric acid, the rotation is instantly changed to $[\alpha]_D = -66.54$, but under the influenc of the heat, soon decreases.[10]

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[1] Schmitt and Cobenzl: Ber. d. chem. Ges., **17**, 1000.
[2] Fischer: *Ibid.*, **23**, 3688.
[3] Schmitt and Cobenzl: *Ibid.*, **17**, 1007.
[4] Ztschr. angew. Chem., 1892, p. 263.
[5] Berthelot: Ann. chim. phys., [3], **55**, 276.
[6] Mitscherlich: J. prakt. Chem., [I], **73**, 65
[7] Scheibler and Mittelmeier: Ber. d. chem. Ges., **23**, 1438.
[8] Bau: Chem. Ztg., **21**, 186.
[9] Scheibler and Mittelmeier.
[10] Michaud: Chem. News, **53**, 232.

20. Trisaccharides and Polysaccharides

Raffinose, Melitose, Melitriose, Gossypose. $C_{18}H_{32}O_{16} + 5H_2O$. Melting-point 118° to 119°. It is found in various vegetable products.

The rotating power was found by several older observers, in pretty close agreement, as

$$[\alpha]_D = +104.5°, \text{ for } t = 20°,$$

and to be but slightly dependent on temperature.

Tollens[1] found that these different products, investigated by the earlier chemists, melitose from eucalyptus manna,[2] raffinose from molasses,[3] gossypose from cottonseed,[4] are identical and show the following values

I. Raffinose from molasses

Water....... $p = 9.817$, $t = 20°$, $d_4^{20} = 1.03278$, $[\alpha]_D = +104.9°$

II. Raffinose from cottonseed:

Water....... $p = 11.158$, $t = 20°$, $d_4^{20} = 1.03279$, $[\alpha]_D = +104.39°$

III. Raffinose from eucalyptus manna

Water....... $p = 9.777$, $t = 20°$, $d_4^{20} = 1.03172$, $[\alpha]_D = +104.44°$

Raffinose is found also in the sugar-beet.

Water........... $p = 2.7616$, $t = 18°$, $[\alpha]_D = 104.96°$[5]

Rischbiet and Tollens give[6]

1. Raffinose from molasses

Water.... $c = 10$, $[\alpha]_D = +102.4$ to $104.9°$

2. Raffinose from cottonseed

Water..... $c = 10$, $[\alpha]_D = 104.4°$

Creydt[7] found:

Water....... $t = 20°$, $c = 16.6$

Raffinose from molasses..... $[\alpha]_D = 104.2°$

" " cotton-seed....... " 104.5

In the inversion of raffinose, two stages may be distinguished. When its solution is warmed gently with weak acid, the rotation sinks to about one-half, but goes no further; but, on the other hand, if the solution is warmed a long time with somewhat stronger acid the rotation is decreased to one-fifth th original value.

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[1] Ann. Chem. (Liebig), **232**, 169.

[2] Berthelot: Ann. chim. phys., [3], **46**, 66.

[3] Loiseau: Compt. rend., **82**, 1058.

[4] Böhm: J. prakt. Chem., [2], **30**, 37.

[5] Lippmann: Ber. d. chem. Ges., **18**, 3089.

[6] Ann. Chem. (Liebig), **232**, 169.

[7] Inaug. Diss., Erlangen, 1888.

Thus, a raffinose solution with $c = 10$, to which 6 cc. o sulphuric acid of sp. gr. 1.0591 had been added, gave ·

After ½ hour's heating to 100° …… $[\alpha]_D = 49.8°$ at 20°
" 1 " " " 80° ….. " $= 49.1$ at 20
" 14 days' standing in the cold …. " $= 53.6$ at 20

But when 10 grams of raffinose was dissolved with 5 cc of sulphuric acid of sp gr. 1.156 and water to make 100 cc., and was then heated five hours to 100°, it showed $[\alpha]_D = +20.07°$ [1]

Scheibler[2] has shown that the specific rotation of raffinose does not change with the concentration or by the addition of alcohol.

Raffinose from beet-sugar
Water … ….. $c = 10$, $t = 17.5°$, $[\alpha]_D = +103.74°$
" ……….. $c = 15$, $t = 17.5$ " $= +103.97$
Alcohol (15 p. c.) · $c = 10$, $t = 17.5$ " $= +103.9$

Raffinose from cottonseed
Water …… … $c = 5$ $t = 17.5$ $[\alpha]_D = +104.0$
" ……….. $c = 10$ $t = 17.5$ " $= +103.9$
" …. …. $c = 15$ $t = 17.5$ " $= +103.95$

Undecylacetylmeletriose, $C_{18}H_{21}O_{16}(C_2H_3O)_{11}$ Crystals with melting-point 99° to 101°.

Alcohol · …… $c = 8.1988$, $t = 17°$, $[\alpha]_D = +92.2°$ [3]

MELEZITOSE, $C_{18}H_{32}O_{16} + 2H_2O$ Rhombic crystals, melting-point, 147° to 148°

For aqueous solutions .

$$[\alpha]_D = +83 + 0.07014p \; [4]$$

Water …… $[\alpha]_D = +88.15°$ [5]

Acetate, $C_{18}H_{21}O_{16}(C_2H_3O)_{11}$. Monoclinic prisms; melting-point, 117°

Benzene …….. $c = 6.243$, $t = 20°$, $[\alpha]_D = 110.44°$ [6]

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[1] Tollens *Loc cit*, Scheibler Ber d chem Ges, **18**, 1782

[2] *Loc. cit*

[3] Scheibler and Mittelmeier · Ber d chem Ges., **23**, 1443

[4] Villiers Bull Soc Chim, **27**, 98, Alechin Russ phys-ch Ges, **21**, 420.

[5] Bourquelot, Hérissey J pharm. chim, [6], **4**, 385

[6] Alechin

LUPEOSE, β-Galactan, $C_{24}H_{42}O_{21} + H_2O(?)$. Amorphous. A preparation dried in hydrogen at 100° gave:

Water........ $p = 5$, $t = 22°$, $[\alpha]_D = +138°$

For three different preparations which were dried at 110° to 115°, these values were found earlier by Steiger:[1]

$[\alpha]_D = +148.7°$, $[\alpha]_D = +149.8°$, $[\alpha]_D = +147.2°$

If we assume that the preparation dried at 100° contains one molecule of water of crystallization, the last three results would agree very well with that calculated for anhydrous lupeose.[2]

TREHALUM, $C_{24}H_{42}O_{21}$, from trehala.

$p = 0.261$ to 0.365, $t = 18°$, $[\alpha]_D = +179°$[3]

GENTIANOSE, $C_{36}H_{66}O_{31}(?)$. Small plates melting at 210°.[4]

An aqueous solution, prepared hot, showed... $t = 18°$, $[\alpha]_D = +65.7°$
" " " " cold, " .. $t = 18°$ " $+33.36$

STACHYOSE, $C_{36}H_{64}O_{32}$. From tubers of *Stachys tubifera*. Crystals

Water... $c = 9$ (amorphous substance), $[\alpha]_D = +146.7°$
" .. $c = 9.5$ (" "), " $+148.8$
" ... $c = 9$ (crystalline "), " $= +148.1$[5]

21. Carbohydrates, $(C_6H_{10}O_5)_n$

AMORPHOUS SOLUBLE STARCH.—From potato starch by heating with glycerol, water, dilute acids, etc.[6]

Water, $c = 2.533$, $[\alpha]_j = +206.8°$[7]
" $c = 2.215$, $t = 17.5$, $[\alpha]_j = 211.50°$, from which $[\alpha]_D = 189.98°$
" $c = 3.995$, $t = 17.5$, " 211.97, " " " 190.24[8]

Other authors give the rotation as $[\alpha]_j = +216°$;[9] $[\alpha]_j = +211°$;[10] $[\alpha]_j = +216°$, $[\alpha]_D = +202°$.[11]

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[1] Landw. Vers. Stat., **36**, 423 and Ztschr. physiol. Chem., **11**, 372.

[2] Schulze, Ber. d. chem. Ges., **25**, 2218.

[3] Scheibler, Mittelmeier: *Ibid.*, **26**, 1331.

[4] Meyer: Ztschr. physiol. Chem., **6**, 135.

[5] Planta and Schulze: Ber. d. chem. Ges., **23**, 1692; **24**, 2705.

[6] Zulkowsky: *Ibid.*, **13**, 1398; Béchamp: Compt. rend., **39**, 653; Musculus, Gruber: *Ibid.*, **86**, 1459.

[7] Zulkowsky: *Loc. cit.*

[8] Salomon: J. prakt. Chem., [2], **28**.

[9] Musculus: Jahresber. (1879), p. 835.

[10] Béchamp: Compt. rend., **39**, 653.

[11] Brown, Morris, Millar: J. Chem. Soc., **71**, 114.

DEXTRINES.

Crystalline Soluble Starch, Amylodextrine.—Formed by t action of cold dilute hydrochloric acid or of hot 90 per cen acetic acid on starch, and separated in crystalline form b freezing the solution.[1] Brown and Morris[2] have determin the molecular weight as $C_{12}H_{22}O_{11} + 6C_{12}H_{20}O_{10}$, and give t rotation as $\alpha_j = + 206.5°$.

Achrodextrine.—According to the statements of differe authors, there are several isomeric dextrines formed under di ferent conditions from starch. Musculus and Gruber[3] di tinguish three kinds

α-Modification	$[\alpha] = + 210°$
β-Modification	" $= + 190$
γ-Modification	" $= + 150$

According to O'Sullivan,[4] there are four different varieti which, however, have the same rotating power. This is give as $[\alpha]_j = + 215°$ to $217°$.

Brown and Heron[5] give $[\alpha]_j = + 216°$.

L. Schulze[6] found the rotation of a carefully purified de trine as $[\alpha]_D = + 186°$

Lustgarten[7] found for a dextrine obtained from dinitr glycogen, $p = 12.175$, $t = 27°$, $[\alpha]_D = + 194°$.

The rotating power of dextrine is increased by acids.[8]

Water	$c = 3.714$,	$t = 17.5°$,	$[\alpha]_j = + 215.06°$
Sulphuric acid, 0.4 p. c....	$c = 1.064$,	$t = 17.5$	" at once) $= + 216.$
			$[\alpha]_j$ (following day) $= + 220.$

An achrodextrine, $(C_{12}H_{20}O_{10})_3 + H_2O$, $[\alpha]_D = + 183°$ described by Lintner and Dull.[9]

Maltodextrine.—By treatment of starch paste with diasta above 65°, $[\alpha]_j = + 169.9$ to $173.4°$;[10] $[\alpha]_j = + 164.2°$.[11]

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[1] Musculus Ztschr Chem , (1869), p 446

[2] Brown and Morris J Chem Soc , **55**, 452

[3] Ztschr physiol Chem , **2**, 188.

[4] J Chem Soc , **35**, 770

[5] Ann Chem (Liebig), **199**, 243.

[6] J prakt. Chem , [2], **28**, 327

[7] Monatsh Chem , **2**, 626

[8] Salomon J prakt Chem , [2], **28**, 42

[9] Ztschr f Brauwes , **17**, 339

[10] Herzfeld Ber d chem Ges , **12**, 2120

[11] Bondonneau Bull. Soc Chim , **25**, 5

Extended investigations on the action of diastase on starch, and especially on malto dextrine, have been carried out by Brown and Morris,[1] also Brown, Morris and Millar.[2]

Artificial Dextrine. From dextrose, sulphuric acid, and alcohol

$[\alpha]_D = +131$ to 134°[3]
$[\alpha]_j = +123°$[4]

Fermentation Gum, dextran, viscose. Produced in the lactic fermentation of cane-sugar.

$[\alpha]_D = +230°$[5]

β-Galactan. From *Lupinus luteus*

Water. ... . $c = 10$, $[\alpha]_D = +148.7°$[6]
" .. . . $c = 3.082$, $t = 15°$, $[\alpha]_D = +148.6°$[7]

Shows no birotation. The rotation changes very little with the concentration.

γ-Galactan. In the sugar-beet

Water ..... $c = 10$, $t = 20°$, $[\alpha]_D = +238°$[8]

α-Galactin. In the seeds of leguminous plants.

$[\alpha]_D = +84.6°$[9]

GLYCOGEN, $C_6H_{10}O_5$, or $C_{36}H_{62}O_{31}$ Found in the liver of man and the herbivora The older statements on the rotation of glycogen vary within very wide limits. Careful observations were made by Kulz.[10] He states that the concentration is without special influence, and he finds as the mean of eighteen readings $[\alpha]_j = +211°$ (greater concentrations than $p = 0.6$ cannot be employed) Landwehr[11] found for the glycogen of dog's liver, for $t = 18°$, $[\alpha]_D = +213.3°$. Further values are.

$[\alpha]_D = +196.33°$[12]
" $= +200.2$[13]

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[1] Ann Chem (Liebig), **231**, 72, J Chem Soc, **55**, 452.
[2] J. Chem Soc, **71**, 72, 109, 115
[3] Musculus and Meyer: Ztschr physiol Chem., **5**, 122
[4] Konig and Schubert. Monatsh. Chem, **6**, 746; **7**, 455
[5] Stohmann and Langbein: J. prakt Chem, [2], **45**, 305
[6] Steiger. Ber d chem Ges, **19**, 829
[7] Schulze and Steiger: Landw Versuchs-Stationen, **36**, 423.
[8] Lippmann Ber. d chem. Ges., **20**, 1001
[9] Muntz Compt. rend, **94**, 453
[10] Jahresber f Thierchemie (1880), p. 81, Arch f. ges Physiologie, **24**, 35
[11] Ztschr. physiol Chem., **8**, 171.
[12] Huppert Ber d chem. Ges., **27**, Ref. 85
[13] Kramer: Ztschr für Biol., **24**, 100.

39

CELLULOSE. According to Levallois[1] this is left-rotating solution of ammoniacal copper hydroxide. But Béchamp[2] giv the direction as variable.

GRAMININ Found in various plants (as *Trisetum alpestr* White powder, melting at 209°.

Water ...... p 5, t 12°, $[\alpha]_D$ 38.89°[3]

INULIN. Found in the roots of different plants. Spheroid crystalline grains; melting-point, 160°.

The older values for the rotation vary between $[\alpha]_D$ 26° and 72.42°. Kiliani[4] found:

Inulin from	Dissolved in	p	t	$[\alpha]_D$
Inula Helenium	Water at 100° diluted with cold water.	1.5122	23°	- 36.66
Dahlia variabil	" "	0.9172	20	37.15
" "	A little potassium hydroxide and then diluted.	1.7456	20	34.10

Lescoeur and Morelle[5] found:

Water ..... $[\alpha]_D$ 36.94°

Haller[6] gives.

Water .... c 7.25, $[\alpha]_D$ 38.8°

Temperature and concentration appear to have no influence

Water .... p 2, $[\alpha]_D$ 37.27°[8]

Inulein.

Water .... c 6.6, $[\alpha]_D$ 29.6°[9]

Pseudo-Inulin.

Water .... c 6.64, $[\alpha]_D$ 32.2°[10]

The last two substances were obtained from *Helianthu tuberosus.*

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[1] Bull. soc chim., **43**, 85.

[2] Ber. d. chem. Ges, **18**, Ref. 113.

[3] Ekstrand and Johanson: *Ibid.*, **21**, 594.

[4] Ann. Chem. (Liebig), **205**, 145.

[5] Bull. soc. chim **32**, 418.

[6] Compt. rend., **116**, 514.

[7] Haller.

[8] Wallach: Ann. Chem. (Liebig), **234**, 368.

[9] Haller: Compt. rend., **116**, 514.

[10] Haller: *Loc. cit.*

IRISIN, Phleïn. In the tubers of *Iris pseud-acorus*. Melting-point, 218°.

Water	p	10,	t	16°,	$[\alpha]_D$	51.54° [1]
	p	10,	t	16,	"	51.15
	p	5,	t	16,	"	-51.55
	p	2,	t	22,	"	-49.90
From Iris	p	5,			$[\alpha]_D$	-52.34° [2]
From Phleum	p	5,			"	-48.12

LEVOSIN. In varieties of grain. Melting-point, 160°.

Water	p	5,	$[\alpha]_D$	-36° [3]

LEVULAN. In beet-sugar molasses. Melting-point, 250°.

Water	c	5 to 30,	t	20°,	$[\alpha]_D$	221° [4]

The temperature is without influence.

SINISTRIN. In the sea onion.

$[\alpha]_D$	41.4° [5]
"	34.6° [6]

TRITICIN In the roots of *Triticum repens*

		$[\alpha]_D$	-43.6° [7]
p	5,	"	-41.07° [8]

22. Gums

ARABIN, Arabic Acid, $C_{12}H_{22}O_{11}$(?) The principal constituent of gum arabic which, however, is a mixture of at least two gums, a right- and a left-rotating variety. Pure arabin may be made from sugar-beets.

$[\alpha]_D$ 98.5° [9]

WOODGUM, Xylan, $C_5H_8O_4$(?). In foliage trees, especially in the birch.

p	1 to 2,	$[\alpha]_D$	84° [10]
$[\alpha]_D$ usually			70° to 85° [11]

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[1] Wallach Ann. Chem (Liebig), **234**, 367

[2] Ekstrand, Johanson: Ber. d. chem Ges., **20**, 3311

[3] Tanret Bull. soc chim., [3], **5**, 724.

[4] Lippmann. Ber d. chem. Ges., **14**, 1511

[5] Schmiedeberg: *Ibid.*, **12**, Ref. 705.

[6] Reidemeister Jahresber. Thierch., 1881, p. 71.

[7] Reidemeister: *Loc. cit.*

[8] Ekstrand, Johanson: Ber. d. chem. Ges., **20**, 3317.

[9] Scheibler: *Ibid.*, **1**, 59

[10] Thomsen: *Ibid.*, **13**, 2168.

[11] Tollens: Handb. d. Kohlenhydrate, II, 202.

Lactosin, $C_{36}H_{62}O_{31} + H_2O$ In the roots of the caryop laceae. Small crystals.

Water.... $p = 2.907$ (for the anhydrous substance), $t = 16°$, d^{1} 1.0128, $[\alpha]_D = +211.7°$ [1]

23. Camphors and Terpenes

In the nomenclature and classification of the following c pounds, the fundamental work of Wallach has been taker the guide. The terpenes are therefore divided into f groups:

A. Aliphatic terpenes,
B. Terpan group,
C. Camphan group,
D. Polyterpenes,

and at the beginning of each group the hydrocarbons will treated, then the alcohols, ketones, and so on

A. ALIPHATIC TERPENES

1. *Hydrocarbons*

Licarene, $C_{10}H_{16}$. Boiling-point, 176° to 178°

d^{0} 0.8445, t $20.2°$, $[\alpha]_D = -7.85°$ [2]

2 *Alcohols*

d-**Licareol**, Coriandrol, $C_{10}H_{17}OH$. Boiling-point, 196° t 198°.

d^{0} 0.8820, $[\alpha]_D = -15.2$ [3]

Boiling-point, 93° to 94° (15.5 mm.).

d^{0} 0.882, $[\alpha]_D^{20.4} = -15.02$ [4]

l-**Licareol**, *l*-Linalool, Aurantiol, Lavendol, Nerolol $C_{10}H_{17}OH$. Boiling-point, 199° to 200°.

$d^{0} = 0.8819$, $d^{15.4} = 0.8662$, $[\alpha]_D^{15.4} = -18.35°$ [5]
$d^{15} = 0.868$, $[\alpha]_D^{15} = -19°$ [6]

Planta and Schulze Ber d chem Ges, **23**, 1692

[2] Barbier Compt. rend., **116**, 993

[3] Barbier *Ibid*, **116**, 1459

[4] Barbier Bull soc chim, [3], **9**, 914

[5] Barbier Compt rend. **114**, 674

[6] Morin *Ibid*, **92**, 99

According to Barbier, licareol and linalool are not identical. He gives:

l-Linalool. Boiling-point, 98° to 100° (14 mm.)

d^{0} 0.8869, $[\alpha]_D^{23.4}$ 11.91°[1]

Boiling-point, 86° to 87° (14 mm.).

d^{20} 0.8622, $[\alpha]_D^{20}$ 19.62°[2]

d-RHODINOL, d-Citronellol, $C_{10}H_{17}OH$.

From *l*-linalool-acetate. Boiling-point, 123° (14 mm.).

d^{0} 0.9021, $[\alpha]_D$ + 1.9°[3]

From citronellal. (Formula given: $C_{10}H_{19}OH$.) Boiling-point, 117° to 118° (17 mm.).

$d^{17.5}$ 0.8565, $[\alpha]_D^{17.5}$ + 4.0

Acetate, $C_{11}H_{20}O_2$. Boiling-point, 119° to 121° (15 mm.).

$d^{17.5}$ 0.8928, $[\alpha]_D^{17.5}$ + 2.37[4]

Geraniol is identical with rhodinol, according to Bertram and Gildemeister;[5] and according to Bouchardat[6] and Tiemann and Semmler[7] licarhodol, also, for which, however, Barbier[8] gives the following constants:

Licarhodol, $C_{10}H_{17}OH$. Boiling-point, 122° (19 mm.).

d^{0} 0.8952, $[\alpha]_D^{20.4}$ - 0.69°

Acetate. Boiling-point, 135° (21.5 mm.)

d^{0} 0.9298, $[\alpha]_D^{19.5}$ 0.28°

l-RHODINOL, l-Citronellol, $C_{10}H_{17}OH$.

From German rose oil. d^{15} 0.8838. Boiling-point, 216° (110° to 120° at 12 mm.).

$[\alpha]_D$ 2.8°[9]

From Turkish rose oil. d^{0} 0.8896. Boiling-point, 124° (16 mm.).

$[\alpha]_D$ 2.62°[10]

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[1] Bull soc chim., [3], 9, 1004

[2] Tiemann: Ber. d. chem. Ges, 31, 834.

[3] Barbier: Bull. soc. chim, [3], 9, 1004.

[4] Tiemann, Schmidt: Ber d. chem. Ges., 29, 906.

[5] J. prakt. Chem., [2], 49, 185.

[6] Compt. rend., 116, 1254.

[7] Ber. d. chem. Ges., 26, 2714

[8] Compt. rend., 116, 1253.

[9] Eckart: Arch. d. Pharm., 229, 355.

[10] Barbier. Compt. rend., 117, 1092.

Boiling-point, 110° (10 mm.).

$d^0 = 0.8731$, $[\alpha]_D = -2.11°$[1]

$d^{20} = 0.8612$, $[\alpha]_D^{20} = -4.33$[2] Formula given as $C_{10}H_{19}OH$.

From Bulgarian rose oil $d^{20} = 0.8785$. Boiling-poi 224.7°.

$[\alpha]_D = -3.22°$[3]

From French geranium oil. $d^0 = 0.8886$. Boiling-poi 124° (14 mm.).

$[\alpha]_D = -2.5°$[4]

3. *Aldehydes*

CITRONELLAL, $C_{10}H_{18}O$. From melissa and citronella oil Boiling-point, 205° to 208° (103° to 105° at 25 mm.).

$d^{17.5} = 0.8538$, $[\alpha]_D^{17.5} = +12.50°$[5]

Boiling-point, 202° to 207°.

$d^{15} = 0.8509$, $[\alpha]_D = +4.8°$[6]

B. TERPAN GROUP

1. *Hydrocarbons*

d-LIMONENE (Citrene, Hesperidene, Carvene), $C_{10}H_{16}$ I oils of orange peel, citron, bergamot, cumin, erigeron, an dill. Boiling-point, 175° to 176°. $d^{20} = 0.846$.

Chloroform .. $p = 14.38$, $d^8 = 1.353$, $[\alpha]_D^8 = +106.8°$[7]

Derivatives. Hydrochloride, $C_{10}H_{16}HCl$. Boiling-point, 97 to 98° (11 to 12 mm.).

$d^{17.8} = 0.973$, $[\alpha]_D^{17.8} = +39.5°$[8]

Tetrabromide, $C_{10}H_{16}Br_4$. Rhombic-hemihedral crystals melting-point, 104°.

Chloroform ... $p = 14.24$, $d^9 = 1.555$, $[\alpha]_D^9 = +73.27°$[9]

α-Nitrosochloride, $C_{10}H_{16}NOCl$. Crystals; melting-point, 103° to 104°.

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[1] Barbier Bouveault Compt rend, **122**, 529

[2] Tiemann, Schmidt Ber d chem Ges, **29**, 923

[3] Markownikoff, Reformatzky J prakt Chem, [2], **48**, 299

[4] Monnet, Barbier Compt. rend, **117**, 1093

[5] Tiemann, Schmidt Ber d chem Ges, **29**, 905

[6] Dodge *Ibid*, **23**, Ref 175 and **24**, Ref 90

[7] Wallach, Conrady Ann Chem (Liebig), **252**, 144

[8] Wallach *Ibid.*, **270**, 189

[9] Wallach Conrady *Ibid*, **252**, 145

Chloroform.... $p = 21.13$, $d^{17} = 1.379$, $[\alpha]_D^{17} = +304.05^\circ$[1]
Chloroform.... $p = 13.30$, $d^{9.8} = 1.441$, $[\alpha]_D^{9.8} = +313.4^\circ$[2]

β-Nitrosochloride. Crystals; melting-point, 105° to 106°.

Chloroform.... $p = 5.339$, $d^{10.5} = 1.476$, $[\alpha]_D^{10.5} = +240.3^\circ$[3]

Benzoyl Nitrosochloride, $(C_{10}H_{13}NOCl)COC_6H_5$. (The same benzoyl compound is formed from the two nitrosochlorides.) Rhombic crystals; melting-point, 109° to 110°.

Acetic ether.... $p = 3.46$, $d^{20.5} = 0.906$, $[\alpha]_D^{20.5} = +101.75^\circ$[4]

α-Nitrolanilide, $C_{10}H_{16}(NO)(NHC_6H_5)$. Monoclinic crystals; melting-point, 112° to 113°.

From α-nitrosochloride:

Chloroform ...... $p = 5.35$, $d^{24} = 1.445$ $[\alpha]_D^{24} = +102.19^\circ$

From β-nitrosochloride

Chloroform .... $p = 7.071$, $d^{19.2} = 1.439$, $[\alpha]_D^{19.2} = +102.25^\circ$

Nitroso-α-nitrolanilide, $C_{10}H_{16}(NO)[N(NO)C_6H_5]$. Crystals; melting-point, 142°.

Ether or benzene ?........ $p = 4.208$, $d^{19.8} = 0.805$, $[\alpha]_D^{19.8} = +46.20^\circ$

β-Nitrolanilide Matted needles; melting-point, 153°.

From α-nitrosochloride

Chloroform... $p = 5.086$, $d^{24} = 1.447$, $[\alpha]_D^{24} = -88.33^\circ$

From β-nitrosochloride

Chloroform · $p = 5.133$, $d^{19.4} = 1.447$, $[\alpha]_D^{19.4} = -89.39^\circ$[5]

α-Nitrolbenzylamine, $C_{10}H_{16}(NO)NH.CH_2C_6H_5$ Needles; melting-point, 93°.

Chloroform	$p = 7.027$,	$d^{9.5} = 1.459$,	$[\alpha]_D^{9.5} = +163.8^\circ$[6]
Hydrochloride in dil alcohol	$p = 3.975$,	$d^{10} = 0.906$,	$[\alpha]_D^{10} = -82.26$
Nitrate " " "	$p = 1.034$,	$d^{11} = 0.900$,	$[\alpha]_D^{11} = -81.0$
d-Tartrate " " "	$p = 1.133$,	$d^{12.5} = 0.900$,	$[\alpha]_D^{12.5} = -49.93$
l-Tartrate " " "	$p = 0.968$,	$d^{10.5} = 0.899$,	$[\alpha]_D^{10.5} = -69.9$

Hydrochlor-nitrolbenzylamine, $C_{10}H_{16}HCl(NO)NHCH_2C_6H_5$ Needles, melting-point, 103° to 104°.

Chloroform . ... $p = 2.403$, $d^{18.5} = 1.47$, $[\alpha]_D^{18.5} = +149.6^\circ$[7]

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[1] Wallach Ann Chem (Liebig), **246**, 224
[2] Wallach, Conrady *Ibid*, **252**, 145
[3] Wallach, Conrady *Loc cit*
[4] Macheleidt Ann Chem (Liebig), **270**, 176
[5] Wallach *Ibid*, **270**, 171.
[6] Wallach, Conrady. *Ibid*, **252**, 148
[7] Wallach *Ibid*, **270**, 192

α-Nitrolpiperidine, $C_{10}H_{16}(NO)NC_5H_{10}$. Rhombic crystals melting-point, 94°.

Chloroform ..... $p = 3.146$, $d^{11} = 1.475$, $[\alpha]^{11}_D = +67.75°$

β-Nitrolpiperidine. Monosymmetric crystals; melting point, 110°.

From α-nitrosochloride:

Chloroform ..... $p = 3.107$, $d^{9.5} = 1.478$, $[\alpha]^{9.5}_D = -60.48°$

From β-nitrosochloride:

Chloroform ..... $p = 2.1104$, $d^{12} = 1.478$, $[\alpha]^{12}_D = -60.37°$[1]

Carvoxime, *Isonitrosoterpene*, $C_{10}H_{14}NOH$. (By splitting of HCl from α- or β-nitrosochloride.) Crystals; melting-point 72°.

Alcohol ...... $p = 4.328$, $d = 0.8025$, $t = 18°$, $[\alpha]_D = -39.34°$

Benzoyl Compound. Crystals, melting-point, 96°.

Chloroform ..... $p = 5.716$, $d^{21} = 1.4455$, $[\alpha]^{21}_D = -26.97°$[3]

Benzoyl-hydrochlorcarvoxime, $C_{10}H_{14}NO.CO\,C_6H_5.HCl$. Crystals, melting-point, 114° to 115°.

Acetic ether...... $p = 11.866$, $d^{20} = 0.926$, $[\alpha]^{20}_D = +9.92°$[4]

l-LIMONENE. In pine needle oil. Boiling-point, 175° to 176°. $d^{20} = 0.846$.

Alcohol ...... $p = 6.126$, $d = 0.795$, $[\alpha]_D = -105.0°$[5]
Chloroform.... $p = 14.3$, $d^{10.5} = 1.353$, $t = 10.5°$, $[\alpha]^{10.5} = -105°$[6]

Derivatives. Hydrochloride. Boiling-point, 97° to 98° (11 to 12 mm.).

$d^{16} = 0.982$, $[\alpha]^{16}_D = -40.0°$[7]

Tetrabromide. Rhombic-hemihedral crystals, melting-point, 104°.

Chloroform ...... $p = 12.85$, $d^{9} = 1.5525$, $[\alpha]^{9}_D = -73.45°$[8]

α-Nitrosochloride. Crystals; melting-point, 103° to 104°.

Chloroform .... $p = 0.993$, $d^{9} = 1.496$, $[\alpha]^{9}_D = -314.8°$

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[1] Wallach, Conrady *Loc cit*

[2] Wallach Ann Chem (Liebig), **246**, 227

[3] Wallach, Conrady *Loc cit*

[4] Wallach, Macheleidt Ann Chem. (Liebig), **270**, 179

[5] Wallach *Ibid*, **246**, 222

[6] Wallach, Conrady *Loc cit*

[7] Wallach Ann Chem (Liebig), **270**, 189

[8] Wallach, Conrady *Loc cit*

β-Nitrosochloride Wooly needles; melting-point, 100°

Chloroform ….. $p = 0.998$, $d^{9.5} = 1.495$, $[\alpha]_D^{9.5} = -242.2°$[1]

Benzoyl Nitrosochloride. Crystals; melting-point, 109° to 110°.

Acetic ether… $p = 4.828$, $d^{19.5} = 0.911$, $[\alpha]_D^{19.5} = -101.84°$[2]

α-Nitrolanilide. Monosymmetric plates; melting-point, 112° to 113°.

Chloroform ….. $p = 7.344$, $d^{19.4} = 1.437$, $[\alpha]_D^{19.4} = -102.62°$

Nitroso Compound. Crystals, melting-point, 142°.

Chloroform .. $p = 4.291$, $d^{19.8} = 0.804$, $[\alpha]_D^{19.8} = -47.82°$

β-Nitrolanilide. Matted needles, melting-point, 153°

Chloroform .. $p = 6.117$, $d^{19.4} = 1.444$, $[\alpha]_D^{19.4} = +87.17°$

Nitroso Compound. Crystals; melting-point, 129° Inactive[3]

α-Nitrolbenzylamine. Needles; melting-point, 93°.

Chloroform ……….. $p = 6.829$, $d^{9.5} = 1.460$, $[\alpha]_D^{9.5} = -163.6°$[4]
Hydrochloride, dil alcohol $p = 3.274$, $d^{10.5} = 0.899$, $[\alpha]_D^{10.5} = +83.06$
Nitrate " " $p = 1.019$, $d^{11.5} = 0.898$, $[\alpha]_D^{11.5} = +81.0$
d-Tartrate " " $p = 1.378$, $d^{12.5} = 0.902$, $[\alpha]_D^{12.5} = +69.6$
l-Tartrate " " $p = 1.119$, $d^{11} = 0.901$, $[\alpha]_D^{11} = +51.0$

Hydrochlornitrolbenzylamine Needles, melting-point, 103° to 104°.

Chloroform… $p = 2.431$, $d^{18.5} = 1.469$, $t = 18.5°$, $[\alpha]_D^{18.5} = -147.4°$[5]

α-Nitrolpiperidine Rhombic crystals, melting-point, 94°.

Chloroform . $p = 3.113$, $d^{11.7} = 1.475$, $[\alpha]_D^{11.7} = -67.60°$

β-Nitrolpiperidine Monosymmetric crystals, melting-point, 110°

Chloroform … $p = 3.051$, $d^{11.5} = 1.476$, $[\alpha]_D^{11.5} = -60.18°$[6]

Carvoxime From the nitrosochloride (or from *d*-carvol) Melting-point, 72°

Alcohol….. $p = 9.846$, $d^{17} = 0.8146$, $[\alpha]_D^{17} = +39.71°$[7]

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[1] Wallach, Conrady *Loc cit*
[2] Macheleidt Ann Chem (Liebig), **270**, 176
[3] Wallach *Ibid*, **270**, 185
[4] Wallach, Conrady *Loc cit*
[5] Wallach Ann Chem (Liebig), **270**, 192
[6] Wallach, Conrady *Loc cit*
[7] Wallach Ann Chem (Liebig), **246**, 227

Benzoyl Compound. Crystals; melting-point, 96°.

Chloroform...... $p = 5.765$, $d^{17} = 1.4545$, $[\alpha]_D^{17} = +26.47°$ [1]

Benzoyl Hydrochlorcarvoxime. Crystals; melting-point, 114° to 115°

Acetic ether. .. $p = 3.157$, $d^{19.7} = 0.907$, $[\alpha]_D^{19.7} = -10.58°$ [2]

Goldschmidt and Freund[3] have prepared the following derivatives from the *d*-carvoxime ($[\alpha]_D = +39.62°$). Solutions in chloroform.

	p	d^t.	t	$[\alpha]_D^t$
Carbanilidocarvoxime.........	2.7205	1.4773	18°	+ 31.67°
Carbo-*o*-toluidocarvoxime	2.7547	1.4755	18	+ 27.40
Carbo-*m*-toluidocarvoxime....	2.7402	1.4763	18	+ 29.79
Carbo-*p*-toluidocarvoxime......	2.7106	1.4729	20	+ 30.75
Benzoylcarvoxime	9.1058	1.4426	18.5	+ 26.64
o-Toluylcarvoxime	9.1942	1.4423	15.5	+ 27.08
m-Toluylcarvoxime	10.0169	1.4363	15.5	+ 26.86
p-Toluylcarvoxime	9.2950	1.4395	15.5	+ 23.44
Phenacetylcarvoxime...	7.7806	1.4378	22	+ 40.63
o-Brombenzoylcarvoxime	5.4687	1.4729	22	+ 25.96
m-Brombenzoylcarvoxime .. .	5.5132	1.4692	23.5	+ 18.24
p-Brombenzoylcarvoxime	5.4965	1.4709	23	+ 14.90
o-Nitrobenzoylcarvoxime	4.5575	1.4647	23	0.0
m-Nitrobenzoylcarvoxime	4.5845	1.4625	23.5	+ 20.68
p-Nitrobenzoylcarvoxime	4.5648	1.4656	22.5	+ 17.33

For further data on carvoxime derivatives, see Goldschmidt and Fischer.[4]

d-SYLVESTRENE, $C_{10}H_{16}$. In Swedish and Russian oil of turpentine. Liquid. Boiling-point, 175° to 176°

$d^{16} = 0.8510$, $[\alpha]_D^{16} = +19.5°$ [5]

Boiling-point 171° $d^{15} = 0.8653$, $[\alpha]_D^{15} = +17°$ [6]

Chloroform..... $p = 14.316$, $d^{10} = 1.351$, $[\alpha]_D^{10} = +66.32°$ [7]

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[1] Wallach, Conrady. *Loc. cit.*

[2] Wallach. Ann. Chem. (Liebig), **270**, 179.

[3] Ztschr. phys. Chem., **14**, 398.

[4] Ber. d. chem. Ges., **30**, 2069.

Atterberg. *Ibid.*, **10**, 1206.

[6] Tilden. J. Chem. Soc., **33**, 80.

[7] Wallach, Conrady. Ann. Chem. (Liebig), **252**, 149.

Derivatives · *Dihydrochloride*, $C_{10}H_{16}$,2HCl. Monosymmetric crystals ; melting-point, 72°.

Chloroform ...... $p = 14\ 20$, $d^{8} = 1.4235$, $[\alpha]^{8}_{D} = +\ 18\ 99°$

Dihydrobromide, $C_{10}H_{16}$,2HBr. Monosymmetric crystals ; melting-point, 72°.

Chloroform ...... $p = 4.359$, $d^{9.5} = 1\ 499$, $[\alpha]^{9.5}_{D} = +\ 17.89°$

Tetrabromide, $C_{10}H_{16}Br_4$. Monosymmetric crystals ; melting-point, 135°.

Chloroform ...... $p = 4.338$, $d^{9.5} = 1.517$, $[\alpha]^{9.5}_{D} = +\ 73.74°$

Nitrolbenzylamine, $C_{10}H_{16}NONH.C_7H_7$ Crystals ; melting-point, 71°.

Chloroform ...... $p = 1\ 908$, $d^{6\ 5} = 1\ 495$, $[\alpha]^{6.5}_{D} = +\ 185.6°$

Nitrolbenzylamine Hydrochloride, $C_{10}H_{16}NONHC_7H_7HCl$. Crystals.

Dil. alcohol...... $p = 1.571$, $d^{7.5} = 0\ 904$, $[\alpha]^{7.5}_{D} = +\ 79\ 2°$ [1]

l-SYLVESTRENE. From *Pinus Abies*. Liquid ; boiling-point, 170.3°.

$d^{10} = 0\ 8664$, $[\alpha]^{10}_{D} = -\ 18\ 3°$ [2]

d-PHELLANDRENE, $C_{10}H_{16}$ In bitter fennel oil, elemi oil and resin. Liquid ; boiling-point, 171° to 172°.

$d^{10} = 0\ 8558$, $[\alpha]^{10}_{D} = +\ 17.64°$ [3]

Derivatives *Diphellandrene*, $C_{20}H_{32}$. Made by heating phellandrene for twenty hours to 140° to 150°. Melting-point, 86°.

Chloroform...... $c = 5\ 65$, $[\alpha]_{D} = +\ 82.9°$ [4]

Nitrite, $C_{10}H_{16}(NO)NO_2$ Melting-point, 94°

Chloroform .... $[\alpha]_{D} = -\ 183.5°$ [5]

d-MENTHENE (hydromenthene), $C_{10}H_{18}$ By splitting off water from *l*-menthol. Liquid , boiling-point, 167.4°

$d^{20} = 0\ 8073$, $[\alpha]^{20}_{D} = +\ 10\ 66°$ ($[\alpha]_{j} = +\ 13\ 25$) [6]

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[1] Wallach, Conrady · *Loc cit*

[2] Kuriloff J prakt Chem , [II], **45**, 126

[3] Pesci Ber d chem Ges , **19**, Ref. 874

[4] Pesci *Loc cit*

[5] Pesci *Loc cit*

[6] Atkinson, Yoshida J Chem Soc , **41**, 53

Boiling-point, 167° to 168°.

d^{20} 0.814, $[\alpha]_D^{20}$ $-26.40°$ [1]

Boiling-point, 167° to 168°.

$[\alpha]_D$ $-53.53°$ [2]

l-MENTHENE. By splitting off hydrochloric acid from the right-rotating menthyl chloride Liquid ; boiling-point, 170° to 171°

d^{20} 0.816, $[\alpha]_D = -34.3°$ [3]

2. *Alcohols*

l-MENTHOL, Menthacamphor, $C_{10}H_{19}OH$. In oil of peppermint. Crystals ; melting-point, 42°. boiling-point, 211.5°.

Alcohol...... $c = 10$, $[\alpha]_D^{18} = -50.1°$ } [4]
" ...... $c = 5$, $[\alpha]_D^{20} = -49.4$ }
" ...... $p = 20$, $d^{20} = 0.8115$, $[\alpha]_D^{20} = -49.35°$ } [5]
" ...... $p = 10$, $d^{20} = 0.8845$, $[\alpha]_D^{20} = -50.59$ }

For menthol of American origin (Michigan), Long gives the following values, holding for $q = 30$ to 92 [6]

Melted .... d_4^{44} 0.8810, $t = 46°$, $[\alpha]_D = -49.86°$
Alcohol ...... t 20° $[\alpha]_D = -48.247 - 0.011108\,q - 0.00001870\,q^2$
Benzene ... t 20° " $-49.511 - 0.025634\,q - 0.0008403\,q^2 + 0.00001102\,q^3$
Glac. acet. acid t 20°, " $-47.711 - 0.006386\,q - 0.00007142\,q^2$

Derivatives · *Carbonate*, $(C_{10}H_{19})_2CO_3$. Mother-of-pearl-like crystals, melting-point, 105°.

Benzene ..... $p = 2.021$ $[\alpha]_D^{21} = -92.52°$ [7]

Urethane, $C_{10}H_{19}O.CO.NH_2$. Rhombic needles, melting-point, 165°.

Chloroform .... $p = 0.58$, $[\alpha]_D^{21} = -85.11°$ [8]

Succinic Acid Monoester, $COOH.C_2H_4.COOC_{10}H_{19}$. Crystals; melting-point, 62°

Benzene ...... $p = 1.375$, $[\alpha]_D^{20} = -59.63°$ [9]

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[1] Sieker Kremers Am. Chem J., 14, 291
[2] Slavinsky J russ chem Ges., 29, 118
[3] Berkenheim Ber d chem Ges., 25, 690
[4] Arth Ann chim phys [6], 7, 438
[5] Beckmann Ann Chem (Liebig), 250, 327
[6] J Am Chem Soc, 14, 149 Chem Centrlbl, 1892 II, 525
[7] Arth *Loc cit* p 470
[8] Arth *Loc. cit*, p 464
[9] Arth *Loc cit* p 473

Succinic Acid Diester, $C_2H_4(COOC_{10}H_{19})_2$. Rhombic octahedra; melting-point, 62°

Benzene....... $p = 1.87$, $[\alpha]_D^{20} = -81.52°$[1]

Phthalic Acid Monoester, $C_6H_4(COOH)(COOC_{10}H_{19})$. Microscopic needles; melting-point, 110°.

Benzene...... $p = 1.575$, $[\alpha]_D^{20} = -105.55°$[2]

Phthalic Acid Diester, $C_6H_4(COOC_{10}H_{19})_2$. Rhombic crystals; melting-point, 133°.

Benzene..... $p = 2.006$, $[\alpha]_D^{20} = -94.72°$[3]

Benzoic Acid Ester, $C_6H_5.COOC_{10}H_{19}$. Crystals; melting-point, 53° to 54°.

Benzene.. . $p = 0.953$, $[\alpha]_D^{20} = -90.92°$[4]
Alcohol ... . $p = 20$, $d^{20} = 0.8312$, $[\alpha]_D^{20} = -86.41°$[5]
Alcohol ... . $p = 20$, $[\alpha]_D = -90.72°$[6]

Goldschmidt and Freund[7] prepared the following derivatives from menthol ($[\alpha]_D = -50.1$)

	p	d_t	t	$[\alpha]_D^t$.
Phenyl carbamic acid ester.	5.6085	1.4486	20°	−77.21°
o-Tolyl " " " .	5.6157	1.4436	21	−65.88
m- " " " " .	5.5791	1.4428	21.5	−71.43
p- " " " " .	5.6177	1.4437	21	−72.30

L. Tschugaeff[8] has made the following determinations:

	d_4^{20}.	$[\alpha]_D^{20}$.
Menthyl formate............	0.9359	−79.52°
" acetate	0.9185	−79.42
" propionate	0.9184	−75.51
" *n*-butyrate	0.9114	−69.52
" *n*-valerate... . ..	0.9074	−65.55
" *n*-caproate	0.9033	−62.07
" *n*-heptylate	0.9006	−58.85
" *n*-caprylate....... ...	0.8977	−55.25

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[1] Arth *Loc cit*, p 482
[2] Arth · *Loc cit.*, p 488
[3] Arth. *Loc cit*, p 486
[4] Arth *Loc cit*, p 481
[5] Beckmann, Pleissner. Ann Chem (Liebig), **262**, 33
[6] Beckmann J prakt Chem, [II], **55**, 17
[7] Ztschr phys Chem, **14**, 397
[8] Ber d. chem Ges, **31**, 360

d-**TERPINEOL**, $C_{10}H_{17}OH$.

a. Liquid ; boiling-point, 213.7° to 217.7° ; $d^{19.5} = 0.9189$.

$$[\alpha]_D^{19.5} = +48.4°\,{}^{1}$$

b. Crystalline, melting-point, 32° ; boiling-point, 120° (20 mm.).

In fused condition, $[\alpha]_D = +19.08°$.

Alcohol.... .. $[\alpha]_D = -85\ 53°$[2]

l-**TERPINEOL**.

a. Liquid ; boiling-point, 217.7° to 220.7° ; $d^{18} = 0.9201$.

$$[\alpha]^{8}_D = -56.2°\,{}^{3}$$

In alcohol-sulphuric acid solution, the rotation sinks very rapidly and may finally disappear entirely.[4]

Boiling-point..... 218° to 223°, $d^0 = 0.961$, $[\alpha]_D = -64\ 05$[5]

b. Solid, melting-point, 32° ; boiling-point, 220°

In melted condition $d^0 = 0.9533$, $[\alpha]_D = -80°$.

Alcohol...... $[\alpha]_D = -92\ 32°$[6]

Melting-point, 32° ; boiling-point, 215° to 218°.

$$[\alpha]_D = -117\ 5\,{}^{7}$$

Derivatives *Formate*, $C_{10}H_{17}OCOH$. Liquid ; boiling-point, 135° to 138° (40 mm.).

$d^0 = 0.9986$, $[\alpha]_D = -69\ 25°$[8]

ISOPULEGOL. Boiling-point, 91° (13 mm.).

$d^{17.5} = 0\ 9154$, $[\alpha]_D^{17.5} = -2\ 66°$[9]

3. *Amine Bases*

d-**MENTHYLAMINE**, $C_{10}H_{19}NH_2$. Liquid ; boiling-point, 206° to 207°. By reduction of the oxime.

Alcohol...... $p = 10.78$, $d^{20}_{0} = 0.8749$, $[\alpha]_D = -9\ 26°$[10]

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[1] Flawitzky Ber d. chem Ges, **20**, 1959

[2] Lafont Ann chim phys, [6], **15**, 204.

[3] Flawitzky Ber d chem Ges, **12**, 2355

[4] Flawitzky

[5] Buchardat, Lafont Compt. rend, **102**, 435

[6] Lafont · Ann chim phys, [6], **15**, 156, 204

[7] Ertschikowsky J russ chem Ges, **28**, 132

[8] Lafont Bull, **49**, 325

[9] Tiemann, Schmidt Ber d chem. Ges, **29**, 903

[10] Negoworoff *Ibid*, **25**, 621

From *l*-menthone by ammonium formate. Liquid; boiling-point, 205°

$d^{6} = 0.866,\quad [\alpha]_D^{6} = +14.71°$[1]

Alcohol .... $c = 12.7016,\quad [\alpha]_D^{\prime} = +8.22°$[2]

Derivatives: The following determinations have all been made by Binz.[3]

Hydrochloride, $C_{10}H_{19}NH_2.HCl$. Prisms, melting-point, 189°.

Water ... . $p = 2.77,\quad d^{15} = 1.0022,\quad [\alpha]_D^{15} = +17.24°$

Ether..... .. $p = 1.71,\quad d^{9} = 0.73,\quad [\alpha]_D^{8} = +8.34°$

The rotation of the solution does not change on standing.

Hydrobromide. Small needles; melting-point, 224°.

Water .... $p = 1.30,\quad d^{14} = 1.03,\quad [\alpha]_D^{14} = +13.83°$

Ether ... ... $p = 1.36,\quad d^{12.5} = 0.729,\quad [\alpha]_D^{12.5} = +5.26°$

Hydroiodide. Crystals, melting-point, 270° (with decomposition).

Water ...... $p = 2.75,\quad d^{14.5} = 1.009,\quad [\alpha]_D^{14.5} = +11.79°$

Formyl Compound, $C_{10}H_{14}NH.COH$. Crystals, melting-point, 116° to 117°

Acetic ether... $p = 1.83,\quad d^{12} = 0.9132,\quad [\alpha]_D^{12} = +50.89°$

" " . $p = 1.809,\quad d^{12} = 0.9128,\quad [\alpha]_D^{12} = +49.98$

Chloroform $p = 5.39,\quad d^{4} = 1.458,\quad [\alpha]_D^{4} = +54.11$

" .. $p = 5.36,\quad d^{5} = 1.459,\quad [\alpha]_D^{5} = +53.96$

Methyl alcohol $p = 7.16,\quad d^{11} = 0.812,\quad [\alpha]_D^{11} = +63.30$

Acetyl Compound, $C_{10}H_{19}NH.COCH_3$. Prisms, melting-point, 166° to 167°.

Acetic ether. $p = 1.77,\quad d^{13} = 0.9124,\quad [\alpha]_D^{13} = +44.71°$

" " $p = 1.42,\quad d^{10} = 0.9132,\quad [\alpha]_D^{10} = +45.48$

Chloroform .. $p = 4.40,\quad d^{5} = 1.468,\quad [\alpha]_D^{5} = +50.57$

" .. $p = 1.89,\quad d^{4} = 1.493,\quad [\alpha]_D^{4} = +51.84$

Methyl alcohol $p = 5.39,\quad d^{10} = 0.810,\quad [\alpha]_D^{10} = +48.80$

Propionyl Compound, $C_{10}H_{19}NH.COC_2H_5$. Crystals, melting-point, 150°.

Acetic ether $p = 1.84,\quad d^{12} = 0.9134,\quad [\alpha]_D^{12} = +40.45°$

" " .. $p = 1.807,\quad d^{12} = 0.913,\quad [\alpha]_D^{12} = +39.56$

Chloroform $p = 5.51,\quad d^{8} = 1.453,\quad [\alpha]_D^{8} = +45.14$

" . $p = 2.7,\quad d^{8} = 1.449,\quad [\alpha]_D^{8} = +46.48$

Methyl alcohol $p = 7.19,\quad d^{9} = 0.8125,\quad [\alpha]_D^{9} = +54.30$

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[1] Wallach, Binz. Ann. Chem. (Liebig), **276**, 324.

[2] Binz. Ztschr. phys. Chem., **12**, 727.

[3] *Ibid.*, **12**, 727.

Butyryl Compound, $C_{10}H_{19}NH.COC_3H_7$. Crystals; melting-point, 105°.

Acetic ether… $p = 1.78$, $d^{13.5} = 0.9114$, $[\alpha]_D^{13.5} = -35.64°$
Chloroform .. $p = 4.88$, $d^{6} = 1.457$, $[\alpha]_D^{6} = -40.59$

l-MENTHYLAMINE, Liquid; boiling-point, 204°. $d_0^{0} = 0.8685$.

Alcoholic solution…….. c ? $[\alpha]_D = -33°$ [1]

Boiling-point, 205°. $d^{7} = 0.860$.

Without solvent. ……… . $[\alpha]_D^{7} = -38.07$ [2]
Alcohol ….. $c = 11.269$, $[\alpha]_D^{7} = -31.90$ [3]

Derivatives. *Hydrochloride* Crystals, decompose above 270°

Water ……. .. $p = 2.99$, $d^{19} = 1.001$, $[\alpha]_D^{19} = -35.66°$
" ……. .. $p = 3.2$ $d^{20} = 0.998$, $[\alpha]_D^{20} = -35.56$

Hydrobromide Needles; decompose above 200°.

Water … .. .. $p = 2.963$, $d^{12} = 1.007$, $[\alpha]_D^{12} = -29.32°$

Hydroiodide. Crystals; decompose above 200°

Water …. . $p = 2.79$, $d^{12} = 1.009$, $[\alpha]_D^{12} = -24.72°$

Formyl Compound. Crystals, melting-point, 102°

Acetic ether.. $p = 2.19$, $d^{10.5} = 0.913$, $[\alpha]_D^{10.5} = -76.44°$
" " … $p = 2.17$, $d^{11} = 0.9135$, $[\alpha]_D^{11} = -76.49$
Chloroform …. $p = 5.25$, $d^{6} = 1.457$, $[\alpha]_D^{6} = -83.78$
" …. $p = 5.22$, $d^{8.5} = 1.4555$, $[\alpha]_D^{8.5} = -82.97$
" … $p = 1.39$, $d^{8.5} = 1.486$, $[\alpha]_D^{8.5} = -82.09$
Methyl alcohol $p = 7.44$, $d^{10} = 0.8131$, $[\alpha]_D^{10} = -83.43$

Acetyl Compound. Crystals; melting-point, 143° to 144°

Acetic ether. . $p = 2.16$, $d^{13} = 0.9118$, $[\alpha]_D^{13} = -76.27°$
" " . $p = 2.06$, $d^{13} = 0.9117$, $[\alpha]_D^{13} = -76.89$
Chloroform . . $p = 5.36$, $d^{9} = 1.4525$, $[\alpha]_D^{9} = -81.73$
" …. $p = 5.34$, $d^{10} = 1.4515$, $[\alpha]_D^{10} = -81.90$
" …. $p = 1.48$, $d^{9} = 1.483$, $[\alpha]_D^{9} = -82.29$
Methyl alcohol $p = 2.52$, $d^{9} = 0.805$, $[\alpha]_D^{9} = -83.64$
" " $p = 7.38$, $d^{10} = 0.8133$, $[\alpha]_D^{10} = -85.67$

Propionyl Compound. Crystals; melting-point, 88° to 89°.

Acetic ether… $p = 2.13$, $d^{13} = 0.911$, $[\alpha]_D^{13} = -67.26°$
Chloroform…. $p = 5.09$, $d^{5} = 1.462$, $[\alpha]_D^{5} = -67.53$
Methyl alcohol $p = 8.93$, $d^{8} = 0.8148$, $[\alpha]_D^{8} = -78.02$
Ethyl alcohol.. $p = 2.6$, $d^{9} = 0.8045$, $[\alpha]_D^{9} = -76.02$

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[1] Andres, Andreeff Ber d chem Ges, 25, 620
[2] Wallach, Binz Ann Chem (Liebig), 276, 323
[3] Binz Ztschr phys Chem, 12, 728

Butyryl Compound Crystals; melting-point, 80°.

Acetic ether... $p = 2.22$, $d^{12} = 0.9122$, $[\alpha]^{12}_D = -63.58°$
" " ... $p = 2.19$, $d^{12.5} = 0.9119$, $[\alpha]^{12.5}_D = -64.75$
Chloroform.... $p = 4.47$, $d^4 = 1.464$, $[\alpha]^4_D = -72.10$
" ... $p = 2.69$, $d^4 = 1.479$, $[\alpha]^4_D = -70.87$

The above determinations all by Binz.[1]

The base, $C_{20}H_{35}N_2Cl$, has been made by Wallach by treatment of iso-*l*-menthonoxime with PCl_5 in chloroform solution. Melting-point, 59° to 60°.

Alcohol ... $p = 2.17$, $d^{20} = 0.7975$, $[\alpha]^{20}_D = -186.35°$ [2]

4. *Ketones*

d-MENTHONE, $C_{10}H_{18}O$ From menthol by oxidation. Liquid; boiling-point, 208°.

$d^{12} = 0.9000$, $[\alpha]^{12}_D = +28.14°$ [3]

Derivatives Oxime, $C_{10}H_{18}NOH$ Thick oil.

Alcohol .... $p = 20$, $d^{20} = 0.8250$, $[\alpha]^{20}_D = -4.85$ [4]
" .... $p = 20$, $d^{?} = 0.8199$, $[\alpha]^{\circ}_D = -9.21$ [5]

Oxime Hydrochloride, $C_{10}H_{18}NOH.HCl$. Melting-point, 95° to 100°

Alcohol .... $p = 10$, $d^{?} = 0.8170$, $[\alpha]^{\circ}_D = -24.48°$ [6]

Dibrommenthone, $C_{10}H_{16}Br_2O$. Melting-point, 79° to 80°

Tetrachloride of carbon ... $p = 3.05$, $[\alpha]_D = +199.4°$ [7]

l-MENTHONE. Liquid, boiling-point 206.3°, 207°

$d^{20} = 0.8972$, $[\alpha]_D = +17.02°$ (calculated from $[\alpha]_j = -21.16$)[8]
$d^{12} = 0.8960$, $[\alpha]^{12}_D = -28.18°$ [9]
$d^{24} = 0.8934$, $[\alpha]^{24}_D = -27.67°$ [10]

Derivatives Oxime Crystals; melting-point, 58°.

Alcohol .... $p = 20$, $d^{20} = 0.8220$, $[\alpha]^{22}_D = +40.7$ to $+42°$
" ... $p = 10$, $d^{20} = 0.7998$, $[\alpha]^{20}_D = -42.51°$

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[1] Ztschr phys Chem, **12**, 727
[2] Wallach Ann Chem (Liebig), **278**, 306
[3] Beckmann *Ibid*, **250**, 338
[4] Beckmann *Loc cit*
[5] Negoworoff Ber d chem Ges, **25**, 620
[6] Beckmann *Loc cit*
[7] Beckmann, Eickelberg Ber d chem Ges, **29**, 418
[8] Atkinson, Yoshida J Chem Soc, **41**, 50
[9] Beckmann *Loc cit*
[10] Binz Ztschr phys Chem, **12**, 727

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Oxime Hydrochloride. Crystals; melting-point, 118° to 119°.

Alcohol .... $p = 10$, $d^{20} = 0.8175$, $[\alpha]_D^{20} = -61.16°$ [1]

Isooxime. Melting-point, 119° to 120°; boiling-point, 295°.

Alcohol .... $p = 24$, $d^{21} = 0.827$, $[\alpha]_D^{21} = -52.25°$ [2]

TANACETONE (Thujone?), $C_{10}H_{16}O$. In the oil of *Tanacetum vulgare* and other oils. Liquid; boiling-point, 84.5° (13 mm.). $d^{20} = 0.9126$, α_D for 2 dm $= +38.5$, from which $[\alpha]_D = +21.1°$ [3]

PULEGONE (Puleone), $C_{10}H_{16}O$. From *Mentha pulegium* (polei oil). Liquid with boiling-point, 222° to 223°.

$d^{23} = 0.9293$, $[\alpha]_D^{23} = +25.35°$ [4]
$d^{20} = 0.9323$, $[\alpha]_D^{20} = +22.89°$ [5]

Derivatives. Oxime, $C_{10}H_{19}NO_2$. Needles; melting-point, 157°.

Alcohol .... $p = 10$, $d^{20} = 0.7998$, $[\alpha]_D^{20} = -83.44°$ [6]

Oxime Hydrochloride, $C_{10}H_{19}NO_2.HCl$. Crystals, melting-point, 117° to 118°.

Alcohol .... $p = 10$, $d^{20} = 0.8268$, $[\alpha]_D^{20} = -32.43°$ [6]

Pulegone Bromide, $C_{10}H_{17}OBr$. Crystals, melting-point, 40.5°.

Alcohol ...... $p = 20$, $d^{20} = 0.8555$, $[\alpha]_D^{20} = -33.88°$ [7]

Oxime, $C_{10}H_{15}NOH$. From pulegone bromide. Crystals, melting-point, 84° to 85°.

Alcohol ...... $p = 20$, $d^{20} = 0.8277$, $[\alpha]_D^{20} = -34.53°$ [8]
" ...... $p = 10$, " $= 0.8114$, " $= -35.15$

d-CARVONE (formerly known as carvol), $C_{10}H_{14}O$. In cumin and dill oils. Liquid; boiling-point, 224°.

$d^{18.5} = 0.960$, $[\alpha]_D^{18.5} = +60.6°$ [9]
$d^{20} = 0.959$, $[\alpha]_D^{20} = +62.2°$ [10]

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[1] Beckmann *Loc cit*

[2] Binz Ann Chem (Liebig), **277**, 157

[3] Semmler Ber d chem Ges, **25**, 3344

[4] Barbier Compt. rend, **114**, 126

[5] Beckmann, Pleissner Ann Chem (Liebig), **262**, 4

[6] Beckmann, Pleissner

[7] Beckmann, Pleissner *Loc cit*, 22

[8] Beckmann, Pleissner. *Loc cit*, 27

[9] Flückiger. Ber d chem. Ges, **17**, Ref 358

[10] Beyer *Ibid*, **16**, Ref 1387

Derivatives · *Hydrogen Sulphide Carvone*, $C_{10}H_{14}O.H_2S$. Crysıls; melting-point, 187°.

Chloroform ...... $c = 10$, $[\alpha]_D^{20} = +5.5°$[1]

Oxime. See under derivatives of *l*-limonene.

l-CARVONE. In curled mint and kuromoji oils. Liquid; oiling-point, 223 to 224°.

$d^{20} = 0.959$, $[\alpha]_D^{20} = -62.46°$[1]

Derivatives · *Hydrogen Sulphide Carvone*. Crystals; meltingoint, 187°.

Chloroform...... $c = 10$, $[\alpha]_D^{20} = -5.5°$[1]

Oxime. See under derivatives of *d*-limonene.

d-IRONE, $C_{18}H_{20}O$. The odoriferous principle of the violet. iquid; boiling-point 144° (16 mm.).

$d^{20} = 0.939$, $[\alpha]_D =$ about $+ 42.6°$[2]

C. CAMPHAN GROUP

1. *Hydrocarbons*

d-CAMPHENE, $C_{10}H_{16}$. Solid; melting-point, 48° to 49°; oiling-point, 160° to 161°;[3] melting-point, 51.2°; boiling-oint, 161° to 163°.[4]

a. From oil of turpentine.

$[\alpha]_D = +17.6$, $([\alpha]_j = +22°)$[5]

b From camphor dichloride. For the fused substance at $= 99.8°$, $d = 0.8345$, and for $t = 83.5$, $\alpha_D = +55.1°$ in a 1 dm. tube.[6] If $d^{83.5}$ be calculated from the data given below for *l*-camphene, we have

$d^{83.5} = 0.8482$, $[\alpha]_D^{83.5} = +64.84°$

Melting-point, 57° to 59°.

$[\alpha]_D = +44.2°$[7]

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[1] Beyer.

[2] Tiemann, Krüger Ber d chem Ges, **26**, 2680

[3] Wallach Ann Chem (Liebig), **230**, 234.

[4] Kachler. *Ibid.*, **197**, 96

[5] Berthelot Jahresber d. Chem (1862), p. 441.

[6] Spitzer Ann. Chem (Liebig), **197**, 129

[7] Montgolfier Compt rend, **85**, 286.

c. From bornyl chloride. $\alpha_D = +19.94°$ for fused substance in 1 dm. tube at 85°. If we take the specific gravity as for l-camphene, we have:

$$d^{85} = 0.8168, \quad [\alpha]^{85}_D = +24.4°\,^{1}$$

d. From spike oil. Liquid; boiling-point, 156° to 160°.

$$[\alpha]_D = +29.10°\,^{2}$$

Derivatives: *Hydrochloride*, $C_{10}H_{16}HCl$.

$$[\alpha]_D = -20.25°\,^{3}$$

Ethylcamphene, $C_{10}H_{15}.C_2H_5$. Liquid, boiling-point, 197.9° to 199.9°.

$$d^{20} = 0.8709, \quad t = 25°, \quad [\alpha]_D = +7.2°\,^{4}$$

Isobutylcamphene, $C_{10}H_{15}.C_4H_9$. Liquid; boiling-point, 228° to 229°.

$$d^{20} = 0.8614, \quad t = 21°, \quad [\alpha]_D = +7.4°\,^{5}$$

l-CAMPHENE, Terecamphene.

a. From *l*-turpentine hydrochloride and alcoholic potash. Melting-point, 45°; boiling-point, 160°.

$$[\alpha]_D = -50.4°, \quad ([\alpha]_j = -63)^{6}$$

Melting-point, 45° to 48°; boiling-point, 156° to 157°. For the fused substance at the temperature *t*, $d = 0.8881 - 0.000839\,t$.

Alcohol.... $q = 62$ to 90, $t = 13$ to $14°$, $[\alpha]_D = -53.80 + 0.03081\,q$

Thus, $p = 20$, $[\alpha]_D = -51.34°\,^{7}$

b. From citronella oil. Liquid; boiling-point, 160°.

$$d^{15} = 0.864, \quad [\alpha]_D = -67°\,^{8}$$

c. From kesso oil. Liquid; boiling-point, 159° to 161°.

$$d^{15} = 0.871, \quad [\alpha]_D = -70.4°\,^{9}$$

Derivatives: *Hydrochloride*, $C_{10}H_{16}.HCl$. Solid; melting-point, 147°.

Alcohol...... $p = 10.5$, $[\alpha]_D = +30.25°\,^{10}$

[1] Kachler Ann Chem (Liebig), **197**, 97

[2] Bouchardat Compt rend., **117**, 1094

[3] Bouchardat. *Loc cit*

[4] Spitzer Ann Chem (Liebig), **197**, 135

[5] Spitzer

[6] Berthelot: Jahresber d Chem (1862), p 457

[7] Riban Ann chim phys, [5], **6**, 357

[8] Bertram, Walbaum J prakt Chem, [2] **49**, 17

[9] Bertram, Walbaum *Loc cit*

[10] Riban: Ann chim phys, [5], **6**, 360

Formate, $C_{10}H_{16}.CH_2O_2$ Liquid; boiling-point, 125° (40 mm.)

$d^0 = 1.0276, \quad [\alpha]_D = + 10.3°$ [1]

Acetate, $C_{10}H_{16}.C_2H_4O_2$. Liquid; boiling-point, 123° to 127° 35 mm.)

$d^0 = 1.002, \quad [\alpha]_D = + 19.45°$ [2]

α-Camphene Phosphonic Acid, $2C_{10}H_{15}.PO_3H_2 + H_2O$.

Alcohol...... $[\alpha]_D = - 119°$ [3]

β-Camphene Phosphonic Acid, $C_{10}H_{15}.PO_3H_2$. Melting-point, 70°.

Ether....... $[\alpha]_D = - 71°$ [4]

d-PINENE, *d*-Terebenthene, Australene, $C_{10}H_{16}$. Is obtained·

a. From American oil of turpentine (*Pinus Australis*, *P. aeda*) The commercial oil shows extremely variable rotation vhich is, in many cases, due to the presence of *l*-pinene from the outhern spruce pine. For the common oil not known to conain the spruce product, there was found $[\alpha]_D = + 9°$ to + 29° The rotation decreases regularly on fractionation.

$d^{20} = 0.9108, \quad [\alpha]_D^{20} = + 14.15°$ [5]

b From Russian oil of turpentine (*Pinus sylvestris*, *P. Abies*). he commercial oil shows $[\alpha]_D + 11.5°$ to 17° (and someimes higher).

For the pure *d*-pinene there is given:

Boiling-point 156.5° to 157.5° $d^{16} = 0.8631, \quad [\alpha]_D^{16} = + 36.3°$ [7]
" " 155.5° " 156.5° . $d^{24.5} = 0.8547, \quad [\alpha]_D^{24.5} = + 32.4°$ [8]
" " 155.5° " 156.5° .. $d^{20} = 0.8600, \quad [\alpha]_D^{20} = + 32.0°$ [9]
" " 161° .... $[\alpha]_D = + 17.1 - 19.4°$ [10]
" " 156° (corr.) at 753 mm. $d_4^0 = 0.8746, \; d_4^{20} = 0.8585$

$[\alpha]_D^{18} = + 45.04°$ [11]

rom cumin oil, b. p. 157° to 158° . .. $d^2 = 0.8404, \quad [\alpha]_D = + 29.46°$ [12]

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[1] Lafont Ann. chim. phys, [6], **15**, 149

[2] Lafont

[3] Marsh, Gardner J Chem Soc., **65**, 36.

[4] Marsh, Gardner

[5] Long. J Anal Appl Chem., **7**, 99 (1893), Chem. Centrbl, 1893, **1**, 835

[6] Landolt. Ann Chem (Liebig), **189**, 315.

[7] Atterberg. Ber d chem. Ges., **10**, 1203

[8] Flawitzky *Ibid*, **11**, 1846

[9] Flawitzky · *Ibid.*, **20**, 1956.

[10] Berthelot · Ann. chim. phys., [3], **40**, 5

[11] Flawitzky J. prakt Chem., [2], **45**, 115

[12] Wolpian · Pharm. Ztschr. für Russland, **35**, 145.

Rimbach[1] found for the influence of different solvents turpentine oil having $[\alpha]_D^{20} = +34.81°$:

Alcohol.......... $q = 10$ to 100, $t = 20°$, $[\alpha]_D = 34.851 - \frac{0.3911\ q}{q - 120.}$

from this for $c = 20$, $[\alpha]_D = 35.63°$

Glac. acet acid... $q = 10$ to 100, $t = 20°$, $[\alpha]_D = 34.889 + 0.001746$

$+ 0.00033528\ q^2$,

from this for $c = 20$, $[\alpha]_D = 36.90°$

These figures are given for the rotations of the oil of tu pentine in mixtures of alcohol and glacial acetic acid:

Comp of the mixture		Turpentine oil in 100 parts of solution Per cent	d_4^{20} of the sol	$[\alpha]_D^{20}$ of the turp oil
Glac acid Per cent	Alcohol Per cent			
84.8	15.2	20.2	0.9653	36.79°
70	30	20.3	0.9349	36.63
50	50	20.6	0.8949	36.44
30	70	20.4	0.8578	36.15
15	85	20.4	0.8298	35.97

Derivatives *Hydrochloride*, $C_{10}H_{16}HCl$ Crystals, melting point 125°.

Alcohol ...... $p = 28.7$, $d^{14} = 0.8496$, $[\alpha]_D^{14} = +30.96°$

" .... $p = 12.24$, $d^{18} = 0.8147$, $[\alpha]_D^{18} = +31.23$

The specific rotation calculated from this, independent o the solvent is:

$$[\alpha]_D = +28.79°\ ^{2}$$

According to Wallach and Conrady[3] the hydrochloride anc the hydrobromide are inactive.

Dibromide, $C_{10}H_{16}Br_2$. Liquid

$d_4^{20} = 1.5943$, $d_4^{40} = 1.5725$, $[\alpha]_D^{12} = +30.5°$ [4]

$d^{15} = 1.1243$, $[\alpha]_D = +7.04°$ [5]

According to Long,[6] the hydrochloride is active. He gives $[\alpha]^{20} = -7.17°$ as the value obtained in experiments with the product from American oil of turpentine. When the nature and sources of the American oils are considered, it is evident that this value cannot be constant. An explanation is thus given for the discordant results of different observers on this point.

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[1] Ztschr phys Chem 9, 701

[2] Flawitzky J prakt Chem [2] 45, 115

[3] Ann Chem (Liebig) 252, 155

[4] Flawitzky Loc. cit.

[5] Wolpian Loc. cit.

[6] J Am. Chem Soc., 21, 637 (1899)

l-PINENE, Terebenthene.

a. French oil of turpentine (*Pinus pinaster*, *Pinus maritima*). The commercial oil shows $[\alpha]_D = -25°$ to $43°$.

b. Venetian turpentine oil (*Pinus larix*). For the commercial oil $[\alpha]_D = -4.2°$ to $4.8°$.

c. Templin oil, oil of pine cones (*Pinus picea*, *Pinus Pumilio*), $[\alpha]_j = -8.2°$ [1] $d^6 = 0.856$, α_j in 1 dm. tube $= -85.2$, $[\alpha]_j = -98.8$. Rectified, $\alpha_j = -92.5$, $[\alpha]_j = -107.6°$.[2]

d. In American oil of turpentine also, *l*-pinene has been found by Long,[3] the specific rotation of which, was in one case found to be $[\alpha]_D = -40.79°$ The *l*-pinene in this case was distilled from fresh oleo resin. It is probable that much of the so-called American oil contains *l*-pinene.[4]

e. In *Asarum Europaeum L* Boiling-point, 162° to 165°. $t = 20°$, $[\alpha]_D = -25.1°$.[5]

Boiling-point 161°.. .. $[\alpha]_D = -33.8$, $([\alpha]_j\ -42.3°)$ [6]
" " 161°. .. d_4^{20} — 0.8629, $[\alpha]_D^{20} = -37.01°$ [7]
" " 156°. d^{10} - 0.8685, $[\alpha]_D$ $-40.3°$ [8]
" " 155°. ... $d^{20} =$ 0.8587, $[\alpha]_D^{20} = -43.4°$ [9]
$[\alpha]_D$ $-44.95°$ [10]
$[\alpha]_D = -49.1°$ [11]

The discordant results are probably explained by the fact that the rotating power of pinene is diminished by oxidation on standing in the air. For example, Landolt found, with a preparation having originally $[\alpha]_D = -37°$, a rotation of

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[1] Jolly, Buchner Ann Chem. (Liebig), **116**, 328

[2] Fluckiger, Berthelot Jahresber, 1855, p. 643

[3] J Anal Appl Chem, **7**, 99 (1893), Chem Centrbl, **1**, 835 (1893), J Am Chem Soc, **16**, 844 (1894)

[4] J. Am Chem Soc, **21**, 637

[5] Petersen Inaug.-Diss (Breslau), Berlin, 1888

[6] Berthelot Ann. chim phys., [3], **40**, 5

[7] Landolt: Ann Chem. (Liebig), **189**, 311

[8] Riban · Ann. chim. phys, [5], **6**, 15.

[9] Flawitzky; Ber d chem Ges., **12**, 2357.

[10] Bouchardat, Lafont · Compt. rend, **102**, 320.

[11] Bouchardat, Lafont: Ann. chim. phys, [6], **16**, 242

$[\alpha]_D = -35.7°$ after the same oil had stood four weeks in a flask with air[1]

With increasing temperature up to 150° the rotation of turpentine oil is decreased according to the following formula[2]

$$[\alpha]_D = 36.61 - 0.00444\,t$$

Derivatives Hydrochloride. Crystals, melting-point, 125°

$$[\alpha]_D = -26.3°\,^{3}$$
$$[\alpha]_D = -30.69°\,^{4}$$

Hydrobromide. Crystals, melting-point, 92°.

$$[\alpha]_D = -24.6°\,^{5}$$
$$[\alpha]_D = -27.802°\,^{6}$$

Phthalimide Compound, $C_6H_4(CO)_2N\,C_{10}H_{17}$ Rectangular plates; melting-point, 90° to 100°.

$$[\alpha]_D = -35°\,38'\,^{7}$$

l-Isoterebenthene, $C_{10}H_{16}$. Made by heating *l*-turpentine oil to 300° Liquid, boiling-point, 175° $d^{22} = 0.8416$

$$[\alpha]_D = -9.45°, \quad [\alpha]_J = -10.87°\,^{8}$$

Boiling-point, 177.5°

$$t = 20°, \quad [\alpha]_D = -8.38°\,^{9}$$

d-ISOTERPENE, $C_{10}H_{16}$. From *d*-terpineol by action of acetic anhydride. Boiling-point, 178.3°.

$$d_4^{20} = 0.8480, \quad [\alpha]_D^{20} = +57.6°\,^{10}$$

l-ISOTERPENE, From *l*-terpineol. Boiling-point, 176.7°

$$d_4^{20} = 0.8529, \quad [\alpha]_D^{20} = -47.5°\,^{11}$$

Boiling-point, 179.3°.

$$d_4^{20} = 0.8486, \quad [\alpha]_D^{20} = -61.0°\,^{12}$$

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[1] Ann Chem (Liebig), **189**, 311

[2] Gernez Ann Ec norm, **1**, 1

[3] Wallach, Conrady Ann Chem (Liebig), **252**, 156

[4] Pesci Gazz chim ital, **18**, 223

[5] Wallach, Conrady *Loc cit*

[6] Pesci *Loc cit*

[7] Pesci Gazz chim ital, **21**, 1 to 4

[8] Riban Ann chim phys, [5], **6**, 218

[9] Barbier Compt rend, **108**, 519

[10] Flawitzky Ber. d chem. Ges, **12**, 2357

[11] Kuriloff J prakt Chem, [2], **45**, 131

[12] Flawitzky Ber d chem Ges, **12**, 2357

l-FENCHENE, $C_{10}H_{16}$. From fenchyl chloride and aniline. Boiling-point = 150°–154°, $d^{18} = 0.8667$

$$[\alpha]_D = -6.46°\ ^{1}$$

2. *Alcohols*

d-BORNEOL, Borneo Camphor, *d*-*α*-Camphol, $C_{10}H_{17}OH$. From *Dryobalanops camphora*. Crystals; melting-point, 198°, boiling-point, 212°. Gives *d*-camphor on oxidation. With two different preparations:

a Acetic ether .... $c = 15.4$, $t = 20°$, $[\alpha]_D = +38.83°$ }[2]
b " " $p = 17.54$, $d^{20} = 0.8876$, $t = 20°$, " $= +38.45$ }

Melting-point, 203°

Alcohol .... $p = 20$, $d^{20} = 0.8280$, $t = 20°$, $[\alpha]_D = +37.44°$[3]

Melting-point, 208.4°.

Alcohol.... $c = 15.4$, $t = 15°$ to 10°, $[\alpha]_D = +37.33°$[4]
Toluene ... $p = 20$, $[\alpha]_D = +38°$ }[5]
Alcohol... $p = 20$, " $= +37$ }

(On artificial borneols, isocamphols, and on the influence of different solvents on the constants of rotation, see below.)

Derivatives *Bornyl Chloride*, $C_{10}H_{17}Cl$. Melting-point, 157°

Acetic ether. . $c = 17.2$, $t = 20°$, $[\alpha]_D =$ about $-23°$[6]

Ethyl Borneol, $C_{10}H_{17}OC_2H_5$. Boiling-point, 205° to 208°

$$d^{0} = 0.9490, \quad [\alpha]_D = +26.3°\ ^{7}$$

Chloral Borneol, $CCl_3CH(OH)OC_{10}H_{17}$. Melting-point, 55° to 56°

Benzene, $c = 15.07$ (½ mol. in 1 liter), $t = 15°$ to 16°, $[\alpha]_D$ $+30.13°$[8]

Bromal Borneol, $CBr_3CH(OH)OC_{10}H_{17}$. Crystals, melting-point, 105° to 109°

Toluene, $c = 21.7$ (½ mol in 1 liter), $t = 15°$ to 16°, $[\alpha]_D = +52.4°$[9]

Acetate, $CH_3CO\ OC_{10}H_{17}$. Crystals, melting-point, 24°

Alcohol ... $c = 19.6$, $t = 15°$ to 16°, $[\alpha]_D$ $+44.97°$[10]

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[1] Gardner and Cockburn: J Chem Soc, **73**, 276.
[2] Kachler Ann. Chem (Liebig), **197**, 88, 90
[3] Beckmann *Ibid.*, **250**, 253
[4] Haller Ann chim. phys, [6], **27**, 394
[5] Beckmann J prakt. Chem, [2], **55**, 31
[6] Kachler Ann. Chem. (Liebig), **197**, 95
[7] Bouchardat, Lafont Compt rend, **104**, 695.
[8] Haller *Ibid.*, **112**, 144.
[9] Minguin: *Ibid.*, **116**, 890.
[10] Haller. *Ibid*, **109**, 29

Benzoate, $C_6H_5CO.OC_{10}H_{17}$. Crystals; melting-point, 25.5°.

Alcohol .... $c = 25.8$, $t = 15°$ to $16°$, $[\alpha]_D = +43\ 92°$[1]

Neutral Succinate, $C_2H_4(COOC_{10}H_{17})_2$. Crystals; melting-point, 83.7°.

Alcohol ...... $c = 39$, $t = 15°$ to $16°$, $[\alpha]_D = +42\ 05°$[2]

Acid Succinate, $C_2H_4.COOH.COOC_{10}H_{17}$. Crystals; melting-point, 58°.

Alcohol .... $c = 25\ 4$, $t = 15°$ to $16°$, $[\alpha]_D = +35\ 59°$[1]

Neutral Phthalate, $C_6H_4(COOC_{10}H_{17})_2$. Crystals; melting-point, 101.1°.

Alcohol ... $c = 43\ 8$, $t = 15°$ to $16°$, $[\alpha]_D = +79\ 54°$[3]

Acid Phthalate, $C_6H_4.COOH\ COOC_{10}H_{17}$. Crystals; melting-point, 164.48°.

Alcohol .... $c = 30\ 2$, $t = 15°$ to $16°$, $[\alpha]_D = +58.38°$[3]

Carbonate, $CO(OC_{10}H_{17})_2$. Melting-point, 220.6°

$[\alpha]_D = +14\ 37°$[4]

Borneol Phenyl Urethane, $C_6H_5NH\ .\ COOC_{10}H_{17}$. Crystals, Melting-point, 137.75°.

Toluene .... $c = 5\ 46$, $t = 15°$ to $16°$, $[\alpha]_D = +34\ 22°$[5]

l-BORNEOL, Valerian Camphor, *l*-α-Camphol. From valerian oil, n'gaï, bang-phien and madder fusel oil. Crystals; melting-point, 204°; boiling-point, 210°. Yields matricaria camphor on oxidation.

Alcohol, $c = 15.4$, $t = 15°$ to $16°$

From valerian oil .... m. p. 208.8°, $[\alpha]_D = -37.77°$[6]
" n'gaï .... " " 209 0, " $= -37\ 77$
" bang-phien .... " " 208 0, " $= -38\ 20$
" madder .... " " 208.1, " $= -37\ 8$

From valerian oil, alcohol, ... $p = 20°$, $d^{20} = 0\ 828°$, $[\alpha]_D^{20} = -37\ 74°$[7]

Toluene ...... $p = 20$, $[\alpha]_D = -38°$[8]
Alcohol .... $p = 20$, " $= -37$

[1] Haller *Loc cit*

[2] Haller Compt rend., 108, 410.

[3] Haller

[4] Haller. Compt rend, 105, 230

[5] Haller: *Ibid*, 110, 149

[6] Haller: Ann chim phys, [6], 27, 395

[7] Beckmann: Ann Chem. (Liebig), 280, 353

[8] Beckmann: J prakt Chem, [2], 55, 31

On the rotation in different solvents, see below under *β-l*-borneol.

Derivatives: Chloral Borneol. Crystals ; melting-point, 55° to 56°.

Benzene....... $c = 15.07$, $t = 15°$ to $16°$, $[\alpha]_D = -30.13°$[1]

Bromal Borneol. Crystals ; melting-point, 105° to 109°.

Toluene. .. $c = 21.7$, $t = 15°$ to $16°$, $[\alpha]_D = -52.4°$[2]

Acetate. Crystals ; melting-point, 24°

Alcohol.. .. $c = 19.6$, $t = 15°$ to $16°$, $[\alpha]_D = -44.02°$[3]

Benzoate. Crystals ; melting-point, 25.5°.

Alcohol .. $c = 25.8$, $t = 15°$ to $16°$, $[\alpha]_D = -44.18°$[4]

Neutral Succinate Crystals ; melting-point, 83.7°.

Alcohol . $c = 39$, $t = 15°$ to $16°$, $[\alpha]_D = -42.39°$[5]

Acid Succinate. Crystals ; melting-point, 58°.

Alcohol . .. $c = 25.4$, $t = 15°$ to $16°$, $[\alpha]_D = -35.94°$[4]

Neutral Phthalate. Crystals ; melting-point, 101.1°.

Alcohol $c = 43.8$, $t = 15°$ to $16°$, $[\alpha]_D = -79.14°$[4]

Acid Phthalate Crystals , melting-point, 164.48°.

Alcohol ... $c = 30.2$, $t = 15°$ to $16°$, $[\alpha]_D = -58.27°$[4]

Carbonate Crystals ; melting-point, 219.4°

$[\alpha]_D = -44.1°$[6]

Borneol Phenyl Urethane. Crystals ; melting-point, 137.25°.

Toluene. . $c = 5.46$, $t = 15°$ to $16°$, $[\alpha]_D = -34.79°$[7]

The following determinations are by L. Tschūgaeff .[8]

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[1] Haller. Compt rend , **112**, 143

[2] Minguin *Ibid*, **116**, 890

[3] Haller · *Ibid.*, **109**, 29.

[4] Haller : *Loc. cit.*

[5] Haller : Compt. rend., **108**, 410.

[6] Haller : *Ibid.*, **105**, 230.

[7] Haller : *Ibid.*, **110**, 149.

[8] Ber d. chem Ges., **31**, 1775.

	d^{20}	$[\alpha]_D^{20}$
l-Borneol formate	1.0058	— 40 46°
" acetate	0 9855	— 44 40°
" propionate	0 9717	— 42.06°
" *n*-butyrate	0 9611	— 39 15°
" *n*-valerate...........	0 9533	— 37 08°
" *n*-caprylate	0 9343	— 31 45°

β-BORNEOL, Isocamphol, Isoborneol.

Montgolfier[1] and Kachler[2] obtained mixtures of two borneols by action of alcoholic potash on the camphors, of which one is stable, the other instable. The first rotates the plane of polarized light in the same direction as does the camphor employed, the second in the opposite direction from that of the camphor, which is reproduced also by oxidation of the mixture. Haller[3] finds that the stable borneols which he designates as *α*-borneols, are identical with the natural borneols, while the instable products, or *β*-borneols, are isomeric. Further peculiarites are shown in the following table ·

		Description	$[\alpha]_D$	By oxidation there is formed
Active	*α*-borneols	right-rotating $\overset{+}{\alpha}$	+ 37 to 38	*d*-Camphor
		left-rotating $\bar{\alpha}$	— 37 to 38	*l*- "
	β-borneols (isoborneols)	right-rotating $\overset{+}{\beta}$	+ 34	*l*- "
		left-rotating $\bar{\beta}$	— 34	*d*- "
Inactive borneols		$\overset{+}{\alpha}$ and $\bar{\alpha}$	..	*r*- "
		$\bar{\beta}$ " $\bar{\beta}$	....	
		$\overset{+}{\alpha}$ " $\bar{\beta}$	....	*d*- "
		$\bar{\alpha}$ " $\overset{+}{\beta}$	....	*l*- "

Haller investigated, further, the influence of different solvents on $\bar{\alpha}$- and $\bar{\beta}$-borneol and found that the rotating power of the latter is changed by the solvent, while that of the first is not altered except by methyl alcohol.

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[1] Ann. chim phys., [5], 14, 13, Compt rend, 84, 90, and 89, 101

[2] Ann. Chem (Liebig), 197, 102

[3] Ann chim phys, [6], 27, 414

$[\alpha]_D$ for $t = 13°$ to $15°$ and $c = 7.7$.

Solvent	Methyl alcohol	Alcohol	Isopropyl alcohol	Isobutyl alcohol.	Acetone.	Ligroin.
$\bar{\alpha}$-Borneol	− 35.93	− 37.33	− 37.23	− 37.23	− 37.87	− 37.12
$\bar{\beta}$-Borneol .. .	− 30.00	− 32.90	− 33.33	− 33.54	− 22.94	− 22.72

Solvent	Acetic ether	Benzene	Toluene	Xylene	*p*-Methyl-propylbenzene
$\bar{\alpha}$-Borneol	− 37.55	− 37.66	− 37.87	− 37.66	− 37.66
$\bar{\beta}$-Borneol	....	− 19.18	− 18.93	− 18.95	− 18.97

d- or *l*-*Isoborneol*

Toluene...... . $p = 20$, $[\alpha]_D = \mp 19°$ } [1]
Alcohol .... $p = 20$, " $= \mp 33°$ }

Derivatives Chloral Borneol. Not crystalline; melting-point, 55° to 56°.

Benzene . . $t = 15°$ to $16°$, $c = 15.07$, $[\alpha]_D = -56.40$ [2]

Borneol Phenyl Urethane. Crystals, melting-point, 130.05°.
Toluene or alcohol..... . $t = 15°$ to $16°$, $c = 5.46$, $[\alpha]_D = -56.77°$ [3]

d-FENCHYL ALCOHOL (Fenchol), $C_{10}H_{17}OH$. Formed by reduction of *l*-fenchone. Crystals, melting-point, 40° to 41°; boiling-point, 200°.

Alcohol..... $p = 9.902$, $d^{21} = 0.809$, $[\alpha]_D^{21} = +10.36°$ [4]

l-FENCHYL ALCOHOL. Formed from *d*-fenchone by reduction. White crystals; melting-point, 40° to 41°; boiling-point, 201°. $d^{50} = 0.933$

Alcohol. . .. $p = 12.91$, $d^{19} = 0.812$, $[\alpha]_D^{19} = -10.35°$ [5]

d-CAMPHENOL, $C_{10}H_{17}OH$. Boiling-point, 196°. By action of glacial acetic acid on *l*-turpentine oil, $[\alpha]_D = +13.9°$

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[1] Beckmann J prakt Chem, [2], **55**, 31
[2] Haller Compt rend, **115**, 143
[3] Haller *Ibid*, **110**, 149
[4] Wallach. Ann. Chem (Liebig), **272**, 104
[5] Wallach *Ibid*, **263**, 145

l-**Camphenol.** Boiling-point about 205° Formed w the *d*-compound, $[\alpha] = -46.9°$.[1]

Isocamphenol, $C_{10}H_{17}.OH$. Obtained from French oil turpentine by heating with benzoic acid. Melting-point, 4 boiling-point, 198° to 199°. $[\alpha]_D = +10.4$.[2]

d-**Pinol Hydrate**, *d*-Sobrerol, $C_{10}H_{16}(OH)_2$ From *d*-t pentine oil Monosymmetric crystals; melting-point, 15

Alcohol .... $c = 5$, $[\alpha]_D = +150°$

l-**Pinol Hydrate**, *l*-Sobrerol. From *l*-turpentine Monosymmetric crystals; melting-point, 150°.

Alcohol .... $c = 5$, $[\alpha]_D = -150°$[3]

3. *Amines*

d-**Bornyl Amine**, $C_{10}H_{17}.NH_2$. Melting-point, 158° to 160 boiling-point, 199° to 200°.

Alcohol ..... $p = 12.5$, $[\alpha]_D = -18.6°$[4]

Forster has recently described the preparation of two born amines One is left-rotating and corresponds to the base Leuckart and Bach, above. This he designates as neoborn amine The other he calls bornyl amine and is right-rotatin The following data are given for the derivatives of the latte

	d	$[\alpha]_D$	$[\alpha]_D$ alcohol	$[\alpha]_D$ benzen
Base $C_{10}H_{17}.NH_2$		− 45.5°	+ 46.2°	+ 57.1
Methyl bornyl amine	0.9075 (21°)	+ 96.8°	+ 81.0°	+ 95.9
Ethyl bornyl amine	0.8947 (20°)	+ 93.0°	+ 75.4°	+ 90.3
n-Propyl bornyl amine.. ...	0.8919 (18°)	+ 89.0°	+ 72.0°	+ 87.1
iso-Propyl bornyl amime ..	0.8861 (14°)	+ 84.0°	+ 63.3°	+ 81.1
Butyl bornyl amine	0.8902 (15°)	+ 81.7°	+ 64.8°	+ 80.3
Dimethyl bornyl amine	..	+ 62.5°	+ 48.7°	+ 59.6
Diethyl bornyl amine	...	....	+ 50.5°	+ 62.6
Formyl bornyl amine	...	− 42.1°	....	..
Acetyl bornyl amine	...	− 42.9°	. ..	....
Benzoyl bornyl amine	....	− 21.8°	....	....

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[1] Bouchardat, Lafont Ann chim phys, [6], 9, 529

[2] Bouchardat Lafont Compt rend, 113, 553

[3] Armstrong Pope J Chem Soc, 59, 315

[4] Leuckart Bach Ber d chem Ges, 20, 104

[5] J Chem Soc 73, 38 75, 934 1149.

Numerical values for other compounds are also given.

d-FENCHYL AMINE, $C_{10}H_{17}NH_2$. From *l*-fenchone. Right-rotating

Derivatives: Benzylidene Compound, $C_{10}H_{17}N : CHC_6H_5$. Crystals; melting-point, 42°.

Methyl alcohol.... $p = 2\ 63$, $d^{19} = 0.796$, $[\alpha]_D^{19} = -62\ 1°$[1]

l-FENCHYL AMINE. From *d*-fenchone oxime. Liquid; boiling-point, 195°. $d^{22} = 0.9095$.

Alcohol .... $p = 14\ 93$, $d^{18} = 0\ 816$, $[\alpha]_D^{18} = -24.63°$[2]
Without solvent... .... $d^{9.5} = 0\ 920$, $[\alpha]_D^{9.5} = -24.89°$[3]

Derivatives: *Formyl Compound*, $C_{10}H_{17}NH.COH$. Crystals; melting-point, 114°. Shows birotation which disappears in twelve hours.

Chloroform . . $p = 3.99$, $d^{11} = 1.466$, $[\alpha]_D^{11} = -36\ 95°$[4]
" . . $p = 3\ 78$, $d^2 = 1\ 485$, $[\alpha]_D^2 = -36.17°$[5]

Acetyl Compound, $C_{10}H_{17}NH.COCH_3$. Crystals; melting-point, 93° to 94°

Chloroform .. .. $p = 4\ 59$, $d^3 = 1.475$, $[\alpha]_D^3 = -46.62°$[6]

Propionyl Compound, $C_{10}H_{17}NH.COC_2H_5$. Crystals; melting-point, 123°

Chloroform... .. $p = 5\ 0$, $d^5 = 1.463$, $[\alpha]_D^5 = -53\ 16°$ } [7]
" .. .. $p = 3\ 94$, $d^{10} = 1\ 466$, $[\alpha]_D^{10} = -52\ 66°$ }

Butyryl Compound, $C_{10}H_{17}NH.CO\,C_3H_7$. Crystals, melting-point, 77 5°

Chloroform...... $p = 1\ 80$, $d^4 = 1\ 489$, $[\alpha]_D^4 = -53\ 08°$ } [7]
" ...... $p = 1\ 793$, " $= 1\ 488$, " $= -53.14°$ }

Benzylidene Compound, $C_{10}H_{17}N\ CHC_6H_5$ Crystals, melting-point, 42°.

Chloroform. . $p = 5.77$, $d^8 = 1\ 453$, $[\alpha]_D^8 = +73.23°$ } [7]
" ...... $p = 5\ 71$, " $= 1\ 455$, " $= +73\ 05°$ }

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[1] Wallach Ann Chem (Liebig), **272**, 106

[2] Wallach, *Ibid*, **263**, 142

[3] Wallach, Binz, *Ibid*, **276**, 318

[4] Wallach, Binz, *Ibid*, **276**, 318

[5] Binz. Ztschr phys. Chem, **12**, 726

[6] Binz. *Loc cit*

[7] Binz

o-Oxybenzylidene Compound, $C_{10}H_{17}N \cdot CHC_6H_4OH$ Crystals melting-point, 94°.

Chloroform...... $p = 4\ 97$, $d^6 = 1\ 471$, $[\alpha]_D^6 = +\ 66\ 59°$ [1]
" ...... $p = 2\ 49$, $d^7 = 1\ 486$, $[\alpha]_D = +\ 65\ 99°$

p-Oxybenzylidene Compound, $C_{10}H_{17}N\ CH.C_6H_4OH$. Crystals; melting-point, 175°. Shows birotation which disappear in eighteen hours

Chloroform.... $p = 1\ 28$, $d^{10} = 1.4905$, $[\alpha]_D^{10} = +\ 72\ 00°$ [1]

o-Methoxybenzylidene Compound, $C_{10}H_{17}N \cdot CH.C_6H_4.OCH_3$ Crystals; melting-point, 56°.

Chloroform.... $p = 5.56$, $d^8 = 1.4605$, $[\alpha]_D^8 = +\ 58\ 98°$ [1]
" .... $p = 5.09$, $d^{10} = 1\ 460$, $[\alpha]_D^{10} = +\ 59\ 42°$

p-Methoxybenzylidene Compound, $C_{10}H_{17}N{:}CH.C_6H_4.OCH_3$ Crystals; melting-point, 54° to 55°.

Chloroform.... $p = 4\ 97$, $d^{11} = 1.4585$, $[\alpha]_D^{11} = +\ 78.10°$ [1]
" . . $p = 4\ 89$, $d^5 = 1\ 468$, $[\alpha]_D^5 = +\ 78\ 01°$

Aminoterebenthene Hydrochloride, $C_{10}H_{15}NH_2.HCl$.

$$[\alpha]_D = -\ 48\ 508°$$ [2]

4. *Ketones*

d-CAMPHOR. Ordinary camphor, Japan or laurel camphor, $C_{10}H_{16}O$. Melting-point, 178.6°,[3] boiling-point, 204°,[4] 209 1° (corr. at 759 mm.).[5] Camphor is active in the fused condition, in solution, and in vapor (see §9) but not in crystalline form

Landolt[6] investigated the rotatory power of camphor in different solvents (see §53). The specific rotation of the pure camphor calculated from the values obtained was found to be, in the mean, $[\alpha]_D = +\ 55.4°$. The following table exhibits the effect of different solvents and the mean value just given is the basis of the calculation. The data refer to $t = 20°$ and $q = 40$ to 90.

[1] Binz

[2] Pesci Gazz chim ital, 18, 219, Ber d chem Ges, 22, Ref 108

[3] Haller Compt rend, 105, 229

[4] Landolt.

[5] Forster Ber d. chem Ges, 23, 2981

[6] Ann Chem (Liebig), 189, 333

Solvent	$[\alpha]_D$	$[\alpha]_D$ for $q = 80$.
Benzene	$55.40 - 0.1664\,q$	$+42.3$
Ethyl alcohol	$55.40 - 0.1780\,q + 0.00037\,q^2$	43.5
Dimethylaniline	$55.40 - 0.1428\,q$	44.0
Acetic acid	$55.40 - 0.1360\,q$	44.5
Methyl alcohol	$55.40 - 0.1630\,q + 0.00066\,q^2$	46.6
Monochloracetic ether	$55.40 - 0.0620\,q$	50.4
Acetic ether	$55.40 - 0.0480\,q$	51.6

We have also the following additional observations:

Ethyl alcohol ... $c = 7$ to 50, $t = 20°$, $[\alpha]_D = 41.982 + 0.11824\,c$ [1]

" " ..... $p = 20$, $t = 20°$, $d^{20} = 0.8255$, $[\alpha]_D = +44.22°$ [2]

" " ...... $q = 50$ to 95, $t = 22.9°$, $[\alpha]_D = 51.945 - 0.0964\,q$ [3]

Alcohol of 80 vol per cent., $c = 2 \quad 6 \quad 10$

$[\alpha]_D = 40.9 \quad 39.25 \quad 38.65$ [4]

Chloroform...... $c = 5$, $[\alpha]_D = 44.2$

Acetic ether. $q = 48$ to 90, $t = 20°$, $[\alpha]_D =$

$56.543 - 0.09065\,q + 0.0004005\,q^2$ [5]

Benzene . $q = 47$ to 90, $t = 20°$, $[\alpha]_D =$

$55.99 - 0.1847\,q + 0.00026902\,q^2$ [6]

75 per cent acetic ether + 25 per cent benzene

$p = 20$, $d^{20} = 0.8907$, $t = 20°$, $[\alpha]_D = +50.12°$

50.5 per cent acetic ether + 49.5 per cent benzene

$p = 20.3$, $d^{20} = 0.9016$, $t = 20°$, $[\alpha]_D = +48.1°$

25.7 per cent. acetic ether + 74.3 per cent benzene

$p = 20$, $d^{20} = 0.8979$, $t = 20°$, $[\alpha]_D = +45.89°$ [6]

Benzene.. $c = 5$ to 40, $t = 20°$ $[\alpha]_D = 39.755 + 0.17254\,c$ [7]

On the quantitative determination of camphor in solutions from the angle of rotation observed, see §184.

The specific rotation of benzene camphor solutions increases with the temperature, but the values bear no simple relations to each other. Forster[8] found

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[1] Landolt Ber d chem Ges, **21**, 191

[2] Beckmann Ann Chem. (Liebig), **250**, 352

[3] Arndtsen, Ann. chim phys, [3], **54**, 418

[4] Hesse Ann Chem. (Liebig), **176**, 119

[5] Rimbach. Ztschr phys Chem. **9**, 698

[6] Rimbach. *Loc. cit*

[7] Forster, Ber d chem Ges., **23**, 2981

[8] *Loc cit*

Temperature	12°	14°	16°	18°	20°	22°	24°	26°
$[\alpha]_D$ for $c =$ 9.997	39.76	40.20	40.64	41.04	41.45	41.86	42.23	42.59
Difference		0.44	0.44	0.40	0.41	0.41	0.37	0.36
$[\alpha]_D$ for $c =$ 19.988			42.54	42.88	43.22	43.56	43.85	
Difference				0.34	0.34	0.34	0.29	

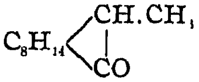
On solutions of camphor in isovaleric acid and caproic acid, see §56

Arndtsen[1] studied the specific rotation of alcoholic camphor solutions with different lights and concentrations and found:

$t = 22.9°$, $q = 50°$ to $95°$

Spectrum line	$[\alpha]$
C	$38.549 - 0.0852\,q$
D............ .	$51.945 - 0.0964\,q$
E	$74.331 - 0.1343\,q$
b..	$79.348 - 0.1451\,q$
F	$99.601 - 0.1912\,q$
e..........	$149.696 - 0.2346\,q$

Transformation Products of d-Camphor.

METHYLCAMPHOR, 
$C_8H_{14}\left\langle\begin{array}{l}CH.CH_3\\ |\\ CO\end{array}\right.$ Crystals; melting-point, 37° to 38°.

Alcohol . ..... $c = 16.6$, $[\alpha]_D = +270.65°$[2]

MONOCHLORCAMPHOR, $C_{10}H_{15}ClO$.

α-Compound. Prismatic crystals; melting-point, 92° to 92.5°; boiling-point, 244° to 247°.

Alcohol .... $[\alpha]_j = +90°$, $([\alpha]_D = +72°)$[3]

Alcohol....... $[\alpha]_D = +95.8°$ from 5 per cent solution.[4]

See the same paper for other camphor derivatives.

[1] Ann chim phys, [3], **54**, 418

[2] Minguin, Compt. rend., **112**, 1371

[3] Cazeneuve *Ibid*, **94**, 1530

[4] Lowry: J Chem Soc, **73**, 569

Derivatives: *Barium Sulphonate*, $(C_{10}H_{14}OCl\,SO_3)_2Ba + 5\frac{1}{2}H_2O$. Crystals.

Water ... . $c = 2\ 081$, $[\alpha]_D^{10} = +46.8°$

Sodium Sulphonate, $C_{10}H_{14}OClSO_3Na + 5H_2O$. Crystals.

Water .... $c = 2.010$, $[\alpha]_D^{10} = +64°$

Sulphochloride, $C_{10}H_{14}OClSO_2Cl$ Crystals, melting-point, 123° to 124°.

Chloroform . .. $c = 4$, $[\alpha]_D^{7} = +110\ 5°$

Sulphonamide, $C_{10}H_{14}OClSO_2NH_2$. Crystals; melting-point, 149.5° to 150.5°.

Alcohol .... $c = 5.066$, $[\alpha]_D^{11} = +90\ 16°$ [1]

β-Monochlorcamphor. Crystals; melting-point, 100°, boiling-point, 230° to 237°.

$[\alpha]_j = +57°$, $([\alpha]_D = +45.6°)$ [2]

γ-Monochlorcamphor. Crystals; melting-point, 124° to 125°; boiling-point, 220°.

$[\alpha]_D = +40°$ [3]

DICHLORCAMPHOR, $C_{10}H_{14}Cl_2O$.

α-Compound. Orthorhombic prisms, melting-point, 96°.

Alcohol or chloroform . $[\alpha]_j = +57\ 3°$, $([\alpha]_D = +45\ 8°)$

β-Compound Mass of crystals, melting-point, 77°.

Chloroform . ... $[\alpha]_j = +60\ 6°$, $([\alpha]_D = +48\ 5°)$ } [4]
Alcohol .. .. " $= +57\ 4°$, (" $= +45\ 9°$) }

TRICHLORCAMPHOR, $C_{10}H_{13}Cl_3O$ Crystals; melting-point, 54°

Alcohol ... $p = 4\ 57$, $[\alpha]_j = +64°$, $([\alpha]_D = +51\ 2°)$[5]

MONOBROMCAMPHOR, $C_{10}H_{15}BrO$

α-Compound. Monoclinic prisms, melting-point, 76°.

Alcohol .... $[\alpha]_D = +139\ 0°$ [6]
" .... " $= +132\ 0°$ [7]
" . . " $= +127\ 7°$ [8]

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[1] Kipping, Pope J. Chem Soc, **63**, 593
[2] Cazeneuve · Compt. rend., **94**, 1530.
[3] Cazeneuve · *Ibid*, **109**, 229
[4] Cazeneuve Bull soc chim., [2], **37**, 454, **38**, 8
[5] Cazeneuve Compt. rend, **99**, 609
[6] Montgolfier Ann. chim phys, [5], **14**, 110
[7] Marsh, Cousins. J Chem Soc, **59**, 969
[8] Haller, Compt. rend, **104**, 66

Derivatives: *Sulphonic Acid*, $C_{10}H_{14}BrOSO_3H$. Crystals, melting-point, 195° to 196°.

Water ...... $c = 2\ 577$, $[\alpha]^{14}_{D} = +\ 88\ 27°$

Potassium Sulphonate, $C_{10}H_{14}BrOSO_3K + 1^1/_2H_2O$. Crystals.

Water .... $c = 4\ 921$, $[\alpha]^{10}_{D} = +\ 71\ 44°$ (hydrated)
" $= +\ 76\ 96°$ (anhydrous)

Sodium Sulphonate, $C_{10}H_{14}BrOSO_3Na + 5H_2O$. Crystals.

Water ..... $c = 4\ 130$, $[\alpha]^{9}_{D} = +\ 63\ 1°$ (hydrated)
" $= +\ 80\ 2°$ (anhydrous) [1]

Water ...... $c = 4\ 305$ (anhydrous), $[\alpha]^{15}_{D} = +\ 88\ 53°$ [2]

Ammoniun Sulphonate, $C_{10}H_{14}BrOSO_3NH_4$ Crystals

Water .... $c = 4\ 600$, $[\alpha]^{9}_{D} = +\ 84\ 78°$ [3]
" .... $c = 4\ 570$, $[\alpha]^{15}_{D} = +\ 87°$ [4]

Barium Sulphonate, $(C_{10}H_{14}BrOSO_3)_2Ba + 5^1/_2H_2O$. Crystals.

Water .... $c = 5.893$, $[\alpha]^{9}_{D} = +\ 64\ 23°$ (hydrated)
" $= +\ 72\ 5°$ (anhydrous) [3]

Magnesium Sulphonate, $(C_{10}H_{14}BrOSO_3)_2Mg$ Crystals

Water ...... $c = 4\ 758$, $[\alpha]^{14}_{D} = +\ 27\ 9°$ [1]

Sulphochloride, $C_{10}H_{14}BrOSO_2Cl$ Crystals; melting-point, 136° to 137°

Chloroform... $c = 5\ 487$, $[\alpha]^{14}_{D} = +\ 131°$ [3]

Sulphonamide, $C_{10}H_{14}BrOSO_2NH_2$. Crystals, melting-point, 145°.

Alcohol ..... $c = 4\ 596$, $[\alpha]^{11}_{D} = +\ 112\ 4°$ [3]

β-Monobromcamphor White powder, melting-point, 61°; boiling-point, 130° (10 mm.)

Alcohol ...... $c = 8.497$, $[\alpha]_D = +\ 29\ 4°$ [5]

Derivatives *Sodium Sulphonate*, $C_{10}H_{14}BrOSO_3Na + 2H_2O$.

Water .... $c = 3\ 422$ (anhydrous), $[\alpha]^{14}_{D} = +\ 12.2°$

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[1] Kipping, Pope J. Chem Soc, 63, 586

[2] Marsh, Cousins: *Loc cit*

[3] Kipping, Pope

[4] Marsh, Cousins

[5] Marsh, Cousins, J Chem Soc, 57, 828

Ammonium Sulphonate, $C_{10}H_{14}BrOSO_3NH_4$.

Water .... $[\alpha]_D = +82^\circ$ [1]

γ-Monobromcamphor. Crystals; melting-point, 144° to 145°.

Alcohol..... ...... $c = 5.5$, $[\alpha]_D = +40^\circ$ [2]

MONOIODOCAMPHOR, $C_{10}H_{15}IO$. Prisms; melting-point, 43° to 44°.

$[\alpha]_D = +160\ 42^\circ$ [3]

CHLORBROMCAMPHOR, $C_{10}H_{14}ClBrO$.

α-Compound Prisms, melting-point, 98°.

Chloroform . .. . $[\alpha]_j = +78^\circ$, $([\alpha]_D = +62.4^\circ)$[4]

β-Compound. Crystals; melting-point, 51.5°.

$[\alpha]_j = +51^\circ$, $([\alpha]_D = +40.8^\circ)$ [5]

For determinations on the halogen derivatives of camphor, see Marsh and Gardner [6]

NITROCAMPHOR, $C_{10}H_{15}NO_2O$

α-Compound Monoclinic prisms; melting-point, 100° to 101°.

Alcohol.	p - 3 33,	$[\alpha]_j = -$ 7 5,	$[\alpha]_D = -$ 6.0°	[7]
Benzene .	$p =$ 0 5,	" $= -$ 140,	" $= -$ 112 6	
Chloroform	$p =$ 0 676,	" $= -$ 140,	" $= -$ 112 6	
"	$p =$ 5 206,	" $= -$ 102,	" $= -$ 96 5	
"	$p =$ 19 978,	" $= -$ 98,	" $= -$ 78 8	

For a lengthy study of nitrocamphor and derivatives, see Lowry [8]

Derivatives *Sodium Compound*, $NaC_{10}H_{14}NO_2O$

Water . $[\alpha]_j = +289$, $([\alpha]_D = +232\ 5^\circ)$

Zinc Compound, $Zn(C_{10}H_{14}NO_2O)_2H_2O$

Alcohol.. . $[\alpha]_j = +275^\circ$, $([\alpha]_D = +221\ 2^\circ)$

Quinine Compound, $C_{20}H_{24}N_2O_2(C_{10}H_{14}NO_2O)_2H_2O$.

Alcohol . . $c = 2\ 72$, $[\alpha]_j = +45\ 9^\circ$, $([\alpha]_D + 36\ 9^\circ)$[9]

[1] Marsh, Cousins J Chem Soc, **59**, 976

[2] Cazeneuve Compt rend **109**, 439

[3] Halle Dissertation, Nancy, 1879

[4] Cazeneuve Bull soc chim, [2], **44**, 116.

[5] Cazeneuve *Ibid*, [2], **44**, 120

[6] Chem News, **74**, 279

[7] Cazeneuve Compt rend, **103**, 275, **104**, 1522

[8] J Chem Soc, **73**, 986 and **75**, 216

[9] Cazeneuve Bull soc chim, **49**, 92

β-Compound. Microscopic plates; melting-point, 83° to 84°.

Alcohol....... $p = 3.33$, $[\alpha]_j = + 7.5$, $([\alpha]_D = + 6.0°)$ [1]
Benzene...... $p = 3.33$, " $= - 75$, (" $= - 60.3°$)

α-CHLORNITROCAMPHOR, $C_{10}H_{14}NO_2OCl$. Prismatic needles; melting-point, 95°.

Alcohol...... $[\alpha]_j = - 6.3°$, $([\alpha]_D = - 5°)$[2]

BROMNITROCAMPHOR, $C_{10}H_{14}NO_2OBr$. Prisms, melting-point, 104° to 105°.

Alcohol..... $c = 1$, $[\alpha]_j = - 27°$, $([\alpha]_D = - 21.7°)$[3]

CAMPHONITROPHENOL, $C_{10}H_{14}NO_2.OH$. Crystals; melting-point, 220°, with decomposition.

Alcohol .... $c = 1.8$, $[\alpha]_D = + 10°$ [4]

Acetyl Derivative, $C_{10}H_{14}NO_2O\ C_2H_3O$. Crystals. melting-point, 115°, with decomposition.

Alcohol......... $c = 2$, $[\alpha]_D = + 4.25°$ [5]

NITROSOCAMPHOR, $C_{10}H_{15}(NO)O$. Crystals; melting-point, about 180°, with decomposition.

Benzene ...... $c = 0.81$, $[\alpha]_D = + 195°$ [6]

CAMPHORSULPHOCHLORIDE, $C_{10}H_{15}OSO_2Cl$. Tetrahedra; melting-point, 137.5°.

Chloroform....... $c = 5.349$, $t = 14°$, $[\alpha]_D = + 128.7°$

CAMPHORSULPHONAMIDE, $C_{10}H_{15}OSO_2NH_2$. Crystals, melting-point, 136° to 137°.

Alcohol.......... $c = 2.252$, $t = 13°$, $[\alpha]_D = + 93.6°$ [7]

CYANCAMPHOR, $C_{10}H_{15}OCN$. Crystals, melting-point, 127° to 128°.

Toluene..... $[\alpha]_D = + 44.68°$ [8]
" .... " $= + 34.4°$ [9]

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[1] Cazeneuve Bull soc chim., 47, 922, Compt rend., 104, 1522
[2] Cazeneuve Compt rend, 96, 589
[3] Cazeneuve. Bull. soc. chim, 42, 69
[4] Cazeneuve Compt rend., 108, 302.
[5] Cazeneuve *Loc. cit*
[6] Cazeneuve Compt rend., 108, 857
[7] Kipping, Pope: J. Chem. Soc, 63, 564
[8] Haller Dissertation, Nancy 1879
[9] Haller Compt rend, 115, 98

Derivatives · *Methyl Compound*, $C_{10}H_{14}OCN.CH_3$. Oil; boiling-point, 170° to 180° (36 mm.).

Toluene .... $c = +9.55$, $[\alpha]_D = +107.69°$[1]

Haller and Minguin[2] have recently isolated two isomeric cyanmethylcamphors with the following characteristics:

β-Compound. Melting-point, 63°; $[\alpha]_D = +150.8°$.

α-Compound. Oil, from which crystals with melting-point 38° to 45° separate. $[\alpha]_D = +90.1°$.

Ethyl Compound, $C_{10}H_{14}OCN.C_2H_5$. Oil; boiling-point, 163° to 165° (21 mm.).

Toluene ..... $c = 10.25$, $[\alpha]_D = +120.71°$

Propyl Compound, $C_{10}H_{14}OCN.C_3H_7$. Crystals; melting-point, 46°, boiling-point, 140° to 150° (20 mm.).

Toluene..... $c = 10.95$, $[\alpha]_D = +126.16°$

Benzyl Compound, $C_{10}H_{14}OCN.C_7H_7$. Crystals, melting-point, 58° to 59°.

Toluene... $c = 13.35$, $[\alpha]_D = +93.62°$

o-Nitrobenzyl Compound, $C_{10}H_{14}OCN\ C_7H_6NO_2$. Needles; melting-point, 104° to 105°.

Toluene..... $c = 15.6$, $[\alpha]_D = +68.37°$[1]

CAMPHOR PINACONE, $C_{20}H_{34}O_2$ Melting-point, 157° to 158°.

Benzene...... $p = 23$, $d_4^{20} = 0.9089$, $[\alpha]_D^{20} = -27.03°$[3]
" ...... $p = 11.62$, " $= 0.8949$, " $= -26.13°$

Derivatives: *Chlor Pinaconan*, $C_{20}H_{31}Cl$. Melting-point, 75°.

Benzene...... $p = 25.47$, $d_4^{18} = 0.9105$, $[\alpha]_D^{18} = +44.17°$[4]
" ...... $p = 74.08$, " $= 0.9436$, " $= +46.50°$

α-Methyl Ether, $C_{20}H_{33}O_2CH_3$. Melting-point, 47°.

Benzene...... $p = 14.15$, $d_4^{20} = 0.8898$, $[\alpha]_D^{20} = -78.33°$[5]
" ..... $p = 56.26$, " $= 0.9123$, " $= -81.80°$

β-Methyl Ether, $C_{20}H_{33}O_2CH_3$. Melting-point, 67°.

Benzene...... $p = 21.70$, $d_4^{20} = 0.8935$, $[\alpha]_D^{20} = -133.50°$[5]

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[1] Haller Compt rend, 113, 55.

[2] Compt rend, 118, 690

[3] Beckmann Ann. Chem. (Liebig), 292, 1.

[4] Beckmann, p. 7.

[5] Beckmann, p. 11.

CAMPHOROXIME, $C_{10}H_{16}$:NOH Monosymmetric prisms; melting-point, 115°.

Alcohol ...... $p = 20$. $d^{20} = 0.835$, $[\alpha]_D^{20} = -42.40°$
" .... $p = 8.3$, " $= 0.812$, " $= -41.38°$

Hydrochloride, $C_{10}H_{16}$:NOH.HCl Crystals, melting-point, 162°, with decomposition

Alcohol ..... $p = 8.3$, $d^{20} = 0.8185$, $[\alpha]_D^{20} = -43.98°$[1]

d-Camphorsulphonate, $C_{10}H_{16}N.OH\ C_{10}H_{15}O.SO_3H + H_2O$. Long needles.

Alcohol .... $c = 1.7508$, $[\alpha]_D^{21} = +4.3°$[2]

See Forster[3] on the esters of camphoroxime

CAMPHORDICHLORIDE, $C_{10}H_{16}Cl_2$ Needles, melting-point, 155° to 155.5°

Acetic ether .... . . $c = 22.34$, $[\alpha]_D = -16°$[4]

CHLORALCAMPHOR, $C_{10}H_{16}O.CCl_3CHO$

$[\alpha]_D = -143$[5]

CHLORALHYDRATE CAMPHOR, $C_{10}H_{16}O\ CCl_3CHOH_2O$ Thick liquid

$d = 1.2512$, $[\alpha]_D = +33.45°$

CHLORALALCOHOLATE CAMPHOR, $C_{10}H_{16}O\ CCl_3CHO\ C_2H_5OH$

$d = 1.1777$, $[\alpha]_D = +36.9°$[6]

BENZYLCAMPHOR BROMIDE, $C_{17}H_{21}BrO$. Melting-point, 82°

$[\alpha]_D = -37.7°$[7]

BENZYLCAMPHOR DIBROMIDE, $C_{17}H_{20}Br_2O$ Melting-point, 92°

$[\alpha]_D = -61°$[8]

MONOCAMPHOR PHENOL, $C_6H_6O.C_{10}H_{16}O$ Liquid, at $-23°$, crystals

$d^0 = 1.0205$, $[\alpha]_D = +20°$[9]

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[1] Beckmann Ann Chem (Liebig) **250**, 352

[2] Pope J Chem Soc, **75**, 1107

[3] J Chem Soc **71**, 1030

[4] Spitzer Ber d chem Ges **11**, 1815

[5] Paschkis Obermayer Pharm Post, **21**, 741
Zeidler Wien Akad Ber 2 Abth, **76**, 253

[7] Haller Minguin Bull soc chim [3], **15**, 958

[8] Haller Minguin

[9] Léger Compt rend, **111**, 109

HEMICAMPHOR PHENOL, $2C_6H_6O.C_{10}H_{16}O$. Liquid; at — 50°, crystals

$d^0 = 1.040, \quad [\alpha]_D = +10.1°$ [1]

MONOCAMPHOR RESORCIN, $C_6H_6O_2.C_{10}H_{16}O$. Crystals; melting-point, 29°.

Alcohol...... $c = 25.1, \quad [\alpha]_D = +22.1°$ [1]

DICAMPHOR RESORCIN, $C_6H_6O_2.2C_{10}H_{16}O$. Sirup; at 0°, crystals

$d^{15} = 1.0366, \quad [\alpha]_D = +25.15°$ [1]

α-NAPHTHOLCAMPHOR, $C_{10}H_8O.C_{10}H_{16}O$. Sirup; at — 16°, crystals

$d^0 = 1.0327, \quad [\alpha]_D = +10.1°$ [1]

β-NAPHTHOLCAMPHOR, $3C_{10}H_8O.5C_{10}H_{16}O$. Liquid

$d^0 = 1.0396, \quad [\alpha]_D = +22.1°$ [1]

SALICYLIC ACID CAMPHOR, $C_7H_6O_3.2C_{10}H_{16}O$. Crystals; melting-point, 60°.

Alcohol........ $c = 20.8, \quad [\alpha]_D = +27.05°$ [1]

CAMPHANIC ACID, $C_{10}H_{14}O_4$

$[\alpha]_D = -7.15°$ [2]

CAMPHINIC ACID, $C_9H_{15}COOH$. Tough mass

$[\alpha]_D = +15.75°$ [3]

CAMPHOLIC ACID, $C_9H_{17}COOH$. Melting-point, 105°

$[\alpha]_D = +49° 8'$ [4]

ISOCAMPHOLIC ACID ETHYL ESTER, $C_9H_{17}COOC_2H_5$. Boiling-point, 228° to 229°.

$d^0 = 0.9477, \quad [\alpha]_D = +21.5°$ [5]

CAMPHOCARBOXYLIC ACID, $C_{10}H_{16}O_3$. Melting-point, 128.7°.

$[\alpha]_D = +66.75°$ [6]

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[1] Léger

[2] Aschan: Act. soc. scient. fennicæ, 21, Nr. 5, p. 1

[3] Montgolfier: Ann. chim. phys., [5], 14, 70

[4] Montgolfier: Loc. cit.

[5] Guerbet: Bull. soc. chim., [3], 13, 769.

[6] Haller: Compt. rend., 105, 229

Derivatives: *Methyl Ester*, $C_{11}H_{15}O_3CH_3$. Boiling-point, 155° to 160° (15 mm.).

Alcohol .... $c = 21$, $[\alpha]_D = + 61.9°$[1]

Methylcamphocarboxylic Acid Methyl Ester, $C_{12}H_{17}O_3CH_3$. Melting-point, 85°.

Alcohol . .... $c = 11.2$, $[\alpha]_D = + 17.25°$[2]

Ethyl Ester, $C_{12}H_{17}O_3C_2H_5$. Melting-point, 60° to 61°.

Alcohol .. .. $c = 11.9$, $[\alpha]_D = + 13.8°$[2]

OXYCAMPHOCARBOXYLIC ACID, $C_8H_{14}COOH.CH_2COOH$. Melting-point, 234°.

Derivatives: *Methyl Compound*, $C_8H_{14}COOH.CH(CH_3).COOH$. Melting-point, 175°.

$[\alpha]_D = + 26.31°$[3]

Monethyl Ester, $C_8H_{14}COOC_2H_5.CH_2COOH$. Liquid; boiling-point, 228° to 230°

$[\alpha]_D = - 51.1°$[4]

Diethyl Ester, $C_8H_{14}COOC_2H_5.CH_2COOC_2H_5$. Liquid; boiling-point, 220° to 230° (160 mm.).

Alcohol .... $c = 27.0$, $[\alpha]_D = - 49.6$ to $+ 50.6°$[5]

Monobenzyl Ester, $C_8H_{14}COOC_7H_7.CH_2COOH$. Oil, boiling-point, 250° to 275° at 10 mm

Alcohol .... $c = 7.6$, $[\alpha]_D = - 52.62°$[6]

Dibenzyl Ester, $C_8H_{14}COOC_7H_7.CH_2COOC_7H_7$. Thick liquid, boiling-point, 260° to 269° at 10 mm.

Alcohol .... $c = 9.85$, $[\alpha]_D = + 35.5°$[7]

Mononitrile (*Cyancampholic Acid*), $C_8H_{14}COOH.CH_2CN$. Crystals; melting-point, 164°.

Alcohol .... $c = 19.5$, $[\alpha]_D = + 64.61°$[8]

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[1] Minguin Compt rend, 112, 1369
[2] Minguin
[3] Haller and Minguin Compt. rend, 118, 691
[4] Haller, Minguin Compt rend, 110, 410
[5] Haller, Minguin.
[6] Minguin: Compt rend, 112, 1454.
[7] Minguin
[8] Minguin: Compt. rend, 112, 51

Mononitrile, Ethyl Ester, $C_8H_{14}COOC_2H_5.CN$. Rhombic crystals; melting-point, 57° to 58°.

Alcohol……… $c = 22.3$, $[\alpha]_D = +57.7°$[1]

Mononitrile, Benzyl Ester, $C_8H_{14}COOC_7H_7.CN$. Crystals; melting-point, 70° to 71°.

Toluene……… $c = 28.5$, $[\alpha]_D = +42.8°$[2]

Mononitrile, Phenyl Ester, $C_8H_{14}COOC_6H_5.CN$. Boiling-point, 267° to 270° at 40 mm.

Alcohol…….. $c = 27.1$, $[\alpha]_D = +26.66°$[3]

Mononitrile, β-Naphthyl Ester, $C_8H_{14}COOC_{10}H_7.CN$. Crystals; melting-point, 117°.

Toluene……… $c = 32.1$, $[\alpha]_D = +17.1°$[4]

Monamide, $C_8H_{14}COOH.CH_2CONH_2$. Melting-point, 205° to 206°.

Alcohol ……… $c = 9.18$, $[\alpha]_D = +63.5°$

d-CAMPHORIC ACID, $C_{10}H_{16}O_4$. Formed by the oxidation of ordinary camphor by nitric acid. Monoclinic crystals. The statements concerning the melting-point vary between 170° and 188°. Thus, 188° (Friedel);[5] 187°, corr. (Riban).[6]

Hartmann[7] has made many observations, the results of which follow.

Solvent	$[\alpha]_D$ for $t = 20°$	Limits	$[\alpha]_D$ for $p = 15$
Abs. alcohol…	$47.178 + 0.01174\,p$	$p = 17$ to 43	$+47.35$
	$48.352 - 0.01174\,q$	$q = 57$ to 83	
Acetone….	$50.689 + 0.00835\,p$	$p = 8$ to 15.5	$+50.81$
	$51.524 - 0.00835\,q$	$q = 84.5$ to 92	
Glac. acetic acid	$45.921 + 0.04904\,p$	$p = 6$ to 16	$+46.66$
	$50.825 - 0.04904\,q$	$q = 84$ to 94	

Derivatives: Salts. Hartmann made the following determinations with aqueous solutions at $t = 20°$. The values for p refer to the anhydrous salts:

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[1] Haller: Compt. rend., 109, 68.

[2] Minguin: *Ibid.*, 112, 51.

[3] Minguin: *Ibid.*, 112, 101.

[4] Minguin: *Ibid.*, 112, 102.

[5] Compt. rend., 108, 984.

[6] *Ibid.*, 80, 1381.

[7] Ber. d. chem. Ges., 21, 223.

Salt	$[\alpha]_D^{12}$	Limits	$[\alpha]_D$ for $p = 10$
$Li_2C_{10}H_{14}O_4$ . . .	$17.750 + 0.23257\,p$	$p = 13$ to 25	$+ 20.08$
	$41\ 007 - 0.23257\,q$	$q = 75$ to 87	
Na_2 "	$14.778 + 0\ 21288\,p$	$p = 11$ to 37	$+ 16\ 91$
	$36\ 066 - 0.21288\,q$	$q = 63$ to 89	
K_2 "	$13\ 081 + 0.13994\,p$	$p = 19$ to 43	$+ 14\ 48$
	$27\ 075 - 0\ 13994\,q$	$q = 57$ to 81	
$(NH_4)_2$ " . . .	$16\ 447 + 0\ 14242\,p$	$p = 11$ to 37	$+ 17.87$
	$30.689 - 0\ 14242\,q$	$q = 63$ to 89	
Mg "	$17\ 824 + 0\ 18779\,p$	$p = 8$ to 16	$+ 19\ 70$
	$36\ 653 - 0\ 18779\,q$	$q = 84$ to 92	
Ca "	$16\ 457 + 0\ 12286\,p$	$p = 3$ to 6	$+ 17.69$
	$28\ 733 - 0\ 12286\,q$	$q = 94$ to 97	
Ba "	$10\ 908 + 0.12980\,p$	$p = 18$ to 36	$+ 12\ 21$
	$23\ 888 - 0\ 12980\,q$	$q = 64$ to 82	

Observations by Thomsen[1] agree very well with these data. He determined the specific rotation of sodium camphorate also, and the effect of addition of excess of sodium hydroxide solution

Landolt[2] gives the following figures ·

Water . . $t = 20°$, $C_{10}H_{14}O_4K_2$ $c = 4$ to 16, $[\alpha]_D = 14\ 39 + 0\ 06\,c$

" . . $t = 20$, " Na_2 $c = 2$ to 9, " $= 16.62 + 0.06\,c$

" . . . $t = 20$, " $(NH_4)_2$ $c = 4$ to 17, " $= 16\ 98 + 0\ 13\,c$

Esters. On the nomenclature of the camphoric acid esters, see Bruhl and Braunschweig.[3]

al-Methyl Ester, C_8H_{14}.COOH.COOCH$_3$. Melting-point, 85° to 86° ; boiling-point, 193° (15 mm.).

$$[\alpha]_D = + 43{\cdot}55°\ ^4$$

o-Methyl Ester, C_8H_{14} COOCH$_3$ COOH. Melting-point, 75° to 76° ; boiling-point, 199° (15 mm.)

$$[\alpha]_D = + 51\ 52°\ ^5$$

Dimethyl Ester, C_8H_{14} COOCH$_3$ COOCH$_3$ Boiling-point, 264° (738 mm.) ; 149.5 (11 mm.).

$$d_4^{20} = 1\ 0747,\quad [\alpha]_D^{22} = + 48\ 16°\ ^6$$

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[1] J prakt Chem , [2], **35**, 157.

[2] "Optisches Drehungsvermögen," 1st ed , p 225

[3] Ber d chem Ges , **25**, 1796

[4] Haller Compt rend , 114, 1516

[5] Haller *Loc cit*

[6] Bruhl *Loc. cit*

$d_4^{17} = 1\ 075$, $[\alpha]_D^{17} = +\ 48\ 32°$ [1]
$[\alpha]_D = +\ 44.4°$ [2]

al-Ethyl Ester, $C_8H_{14}.COOH\ COOC_2H_5$. Melting-point, 57°, boiling-point, 207° to 208° (21 mm.).

$d^0 = 1\ 1004$, $[\alpha]_D = +\ 23.9°$ [3]

o-Ethyl Ester, $C_8H_{14}.COOC_2H_5\ COOH$. Boiling-point, 216° to 219° (30 mm).

$d^0 = 1\ 1133$, $[\alpha]_D = +\ 39\ 18°$ [4]

al-Methyl-o-ethyl Ester, $C_8H_{14}.COOCH_3.COOC_2H_5$. Boiling-point, 277° (746 mm.); 169.5° (33 mm.).

$d_4^{22} = 1\ 0528$, $[\alpha]_D^{22.2} = +\ 38\ 43°$ [5]

o-Methyl-al-ethyl Ester, $C_8H_{14}.COOC_2H_5\ COOCH_3$. Boiling-point, 278° (747 mm.); 175° (38 mm.)

$d_4^{22} = 1\ 0448$, $[\alpha]_D^{22.2} = +\ 45.49°$ [6]

Diethyl Ester, $C_8H_{14}\ COOC_2H_5.COOC_2H_5$. Boiling-point, 285° to 286° (750 mm.); 155° (12 to 14 mm)

$d_4^{19\ 6} = 1\ 0301$, $[\alpha]_D^{19\ 6} = +\ 36\ 30°$ [6]
$d^0 = 1\ 0495$, $[\alpha]_D = +\ 37\ 7°$ [7]

Phenylhydrazide, $C_8H_{14}(COO)_2\ N.NHC_6H_5$ Melting-point, 119°.

$[\alpha]_D = +\ 16\ 41°$ [8]

Compound $C_{22}H_{34}O_7$ From *o*-methyl ester and phenyl cyanate. Melting-point, 78° to 79°

$[\alpha]_D = +\ 49\ 33°$ [9]

Compound· $C_{22}H_{34}O_7$ From *al*-methyl ester and phenyl cyanate Melting-point, 62°

$[\alpha]_D = +\ 81\ 45°$ [9]

Camphoric Anhydride, $C_{10}H_{14}O_3$ Melting-point, 217°. According to Hartmann,[1] it is inactive in benzene or chloroform solution. Other authors have observed left rotation.

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[1] Walker J Chem Soc, **61**, 1091
[2] Haller *Loc cit*
[3] Friedel Compt rend, **113**, 829
[4] Friedel *Loc cit*
[5] Bruhl Ber d chem Ges, **25**, 1799
[6] Bruhl *Loc cit*
[7] Friedel Compt rend, **113**, 829
[8] Haller *Ibid*, **114**, 1516
[9] Haller *Ibid*, **115**, 19

Benzene ...... $p = 0.7705$, $[\alpha]_D = -7.12°$ [2]
Benzene .... $[\alpha]_D = -3.7°$ [3]
Benzene .... $[\alpha]_j = -3.68°$ } [4]
Chloroform .. .. " $=$ 0.0° }

Amide, $C_{10}H_{14}O_2.N_2H_4$. Melting-point, 241° to 242°.

Chloroform. ... ... $[\alpha]_D = -10.6°$ [5]

Chloride, $C_{10}H_{14}O_2Cl_2$ Liquid; boiling-point, 140° (15 mm.).

$[\alpha]_D = -3.0$ to $-3.6°$ } [3]
Benzene....... " $= -7.1$ to $-8.3°$ }

α-Aminic Acid, $C_8H_{14}(CONH_2)COOH$ Melting-point, 176° to 177°

Alcohol...... $[\alpha]_D = +45°$

β-Aminic Acid, $C_8H_{14}(CONH_2)COOH$. Melting-point, 180° to 181°.

Alcohol...... $[\alpha]_D = +60°$

Nitrilic Acid, *Cyanolauronic Acid*, $C_8H_{14}(CN)COOH$. Melting-point, 151° to 152°.

$[\alpha]_D = +67.5°$ [6]

Bromcamphoric Anhydride.

Chloroform...... $[\alpha]_j = -21.1°$

Chlorcamphoric Anhydride.

$[\alpha]_j = -16.3°$ [4]

Campholide, $C_{10}H_{16}O_2$. Melting-point, 210° to 212°

$[\alpha]_D = +5.61°$ [7]

ISOCAMPHORIC ACID, $C_{10}H_{16}O_4$. Melting-point, 170°; boiling-point, 294°.

Alcohol........ $[\alpha]_D = -48.09$ [3]
Alcohol..... .. $[\alpha]_D = -46°$ [8]
Alcohol........ $[\alpha]_j = -48.3°$ [9]

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[1] Ber d chem Ges., **21**, 223
[2] Montgolfier Ann chim. phys, [5], **14**, 86
[3] Marsh Chem. News, **60**, 307.
[4] Aschan Act soc scient fennice, **21**, Nr 5, p 1
[5] Guareschi Centralbl, 1887, p 1355
[6] Hoogewerff, Dorp Rec. trav chim Pays-Bas, **14**, 252
[7] Haller Bull soc. chim, [3], **15**, 984.
[8] Friedel Compt rend., **108**, 980
[9] Aschan *Loc cit*

Derivatives *o-Ethyl Ester*, $C_{10}H_{15}O_4 \cdot C_2H_5$. Melting-point, 195° to 197° (18 mm.).

$$d = 1.1159, \quad [\alpha]_D = -49.51^\circ$$ [1]

Diethyl Ester, $C_{10}H_{14}O_4(C_2H_5)_2$. Boiling-point, 165° (25 to 28 mm.).

$$d = 1.0473, \quad [\alpha]_D = -48.53^\circ$$ [2]

CHOLECAMPHORIC ACID (Choloidanic acid), $C_{10}H_{16}O_4$. From cholic acid by action of nitric acid. Crystals, which turn brown at 270° without melting

Absolute alcohol .. .. $c = 6.42$, $[\alpha]_D^{18} = -56.17^\circ$
Glacial acetic acid. .... $c = 1.44$, " $= +57.83^\circ$

The specific rotation in alcoholic solution is independent of the concentration.[3]

CAMPHORONIC ACID, $C_6H_{11}(COOH)_3$. Melting-point, 158° to 159°.

Water ...... $p = 10$, $[\alpha]_j^{19.5} = -26.9^\circ$, $([\alpha]_D^{19.5} = -23.91^\circ)$[4]

CAMPHOLYTIC ACID, $C_8H_{13}COOH$. Oil; boiling-point, 240° to 242°.

$$d_4^{15} = 1.017, \quad [\alpha]_D^{10} = -5^\circ$$ [5]

Derivatives. *Ethyl Ester*. Oil, boiling-point, 212° to 213°.

$$d_4^{15} = 0.962, \quad [\alpha]_D^{10} = +5.04^\circ$$ [6]

CAMPHOTHETIC ACID, $C_{16}H_{28}(COOH)_2$.

Derivatives. *Diethyl Ester*. Liquid, boiling-point, 135° to 140° (15 mm.)

$$d_4^{18} = 1.019, \quad [\alpha]_D^{10} = +30.6^\circ$$ [7]

DIHYDROXYCYANCAMPHOLYTIC ACID, $C_8H_{14}COOH \cdot CN$. Melting-point, 109 to 111°

Alcohol ..... $[\alpha]_D = +18.20^\circ$ [8]

DICAMPHOR. Melting-point, 165° to 166°

Benzene . ... $p = 5$, $[\alpha]_D^{27} = -28.07^\circ$
Alcohol .. .. $p = 2.5^\circ$, $[\alpha]_D^{22} = -4.05^\circ$

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[1] Friedel Compt rend, 113, 831
[2] Friedel
[3] Latschinoff Ber d chem Ges, 13, 1052
[4] Ossian, Aschan *Ibid*, 28, 16
[5] Walker J. Chem Soc, 63, 499
[6] Walker *Loc. cit*, 498
[7] Walker. J Chem Soc, 63, 504
[8] Hoogewerff, Dorp Rec trav. chim Pays-Bas, 14, 252

Dicamphandihydropyridazine: Melting-point, 155° to 156°.

Benzene . . . . $p = 5$, $[\alpha]^{22}_D = +118.13°$

Dicamphanhexandion. Melting-point, 192° to 193°.

Benzene . . . . $p = 3.5$, $[\alpha]^{27}_D = +331°$
Alcohol . . . . . . $p = 2.9$, $[\alpha]^{24}_D = +381°$

Dicamphanhexanazine: Melting-point, 201° to 202°

Benzene . . . . $p = 5$, $[\alpha]^{27}_D = +51.1°$

Dicamphanhexadienperoxide.

Benzene . . . . $p = 3.5$, $[\alpha]^{16}_D = +296°$
Alcohol . . . . $p = 2.9$, $[\alpha]^{15}_D = +345.11°$

Camphancamphoric Acid Melting-point, 224° to 225°

Alcohol . . . . $p = 4.75$, $[\alpha]^{12.6}_D = +93.6°$

α-Dicamphandiacidanhydride: Melting-point, 143° to 144°.

Alcohol . . . . $p = 1.1$, $[\alpha]^{14}_D = -142°$[1]

l-CAMPHOR Matricaria camphor. Found in the oil of *Matricaria Parthenium*, and may be made by oxidation of *l*-borneol Melting-point, 178.6°;[2] boiling-point, 204°; $d_{18} = 0.9853$. The specific rotation in alcoholic solution for red light ($\lambda = 635$), and $p = 10$ was found as $[\alpha]_r = -33°$; that is, in agreement with the rotation of laurel camphor. The formula for the specific rotation of the latter,[3] $[\alpha]_r = 45.25° - 0.1369\,q$ gives for $p = 10$ ($q = 90$), $[\alpha]_r = +32.9°$[4]

Alcohol . . . . $p = 20$, $d^{20}_{20} = 0.8255$, $[\alpha]^{20}_D = -44.22°$[5]

Transformation Products of l-Camphor

l-CAMPHORPINACONE Right-rotating.

Benzene. . . $p = 23.74$, $d^{20}_4 = 0.9075$, $[\alpha]^{20}_D = +26.52°$[6]

l-CAMPHOROXIME. Melting-point, 115°.

Alcohol . . . . . . $p = 20$, $d^{20}_{20} = 0.835$, $[\alpha]^{20}_D = +42.51°$ } [7]
" . . . . $p = 8.3$, " $= 0.812$, " $= +41.38$ }

Hydrochloride, $C_{10}H_{16}NOH.HCl$ Melting-point, 162°

Alcohol . . . . . . $p = 8.33$, $d^{20}_{20} = 0.8185$, $[\alpha]^{20}_D = +42.52°$[8]

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[1] Oddo Gazz chim. ital., **27**, X, 149
[2] Haller: Compt rend., **105**, 229
[3] Biot Ann chim phys, [3], **36**, 301
[4] Chantard J pharm Chem, [3], **44**, 13. Jahresber, 1863, p. 555
[5] Beckmann Ann Chem. (Liebig), **250**, 253
[6] Beckmann *Ibid*, **292**, 25
[7] Beckmann *Loc cit*
[8] Beckmann

l-CAMPHANIC ACID.

$[\alpha]_J = + 7°$[1]

l-CAMPHOCARBOXYLIC ACID Melting-point, 128.7°.

$[\alpha]_D = - 66.86°$[2]

l-CAMPHORIC ACID. Resembles *d*-camphoric acid and rotates as strongly to the left as the latter does to the right.[3]

Absolute alcohol........... $[\alpha]_J = - 49.5°$[4]

l-Bromcamphoric Acid.

Chloroform............. ... $[\alpha]_J = + 21\ 6°$[4]

l-ISOCAMPHORIC ACID. Resembles the left-rotating isocamphoric acid from *d*-camphoric acid and rotates as strongly to the right.

$[\alpha]_J = + 48.6°$[4]

l-CAMPHORONIC ACID.

Water ..... $p = 10$, $[\alpha]_J^{19\ 5} = + 27.05$, ($[\alpha]_D^{19\ 5} = + 24\ 04°$)[5]

d-FENCHONE, $C_{10}H_{16}O$. From oil of fennel Crystals, melting-point, 5° to 6°; boiling-point, 192° to 193°, $d^{19} = 0\ 9465$.

a. Direct from fennel oil.

Alcohol.. . $p = 8.333$, $d^{18} = 0\ 8045$, $[\alpha]_D^{18} = + 71\ 97°$

b. From fenchyl alcohol

Alcohol.. . $p = 12\ 93$, $d^{19} = 0\ 8090$, $[\alpha]_D^{19} = - 71\ 70°$[6]

Derivatives Oxime, $C_{10}H_{16}NOH$ Crystals, melting-point, 161°.

Alcohol.... $p = 1\ 14$, $d^{19} = 0.793$, $[\alpha]_D^{19} = - 65\ 94°$[6]
Acetic ether $p = 2\ 72$, $d^{14\ 5} = 0.911$, $[\alpha]_D^{14\ 5} = - 52\ 61°$
" " $p = 2.24$, $d^{14} = 0.9115$, $[\alpha]_D^{14} = - 52\ 28$
" " $p = 1\ 60$, $d^{12\ 5} = 0.9121$, $[\alpha]_D^{12\ 5} = - 51\ 62$ }[7]

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[1] Aschan Act soc scient. fennice, **21**, Nr 5, p 1

[2] Haller Compt. rend, **105**, 229

[3] Chantard *Ibid*, **37**, 166, Jahresber, 1853, p 430 Jungfleisch Compt. rend, **110**, 791

[4] Aschan *Loc cit*

[5] Ossian, Aschan Ber d chem Ges, **28**, 16

[6] Wallach Ann Chem (Liebig), **263**, 132

[7] Binz Ztschr phys Chem, **12**, 725

Oxime Anhydride, $C_{10}H_{15}N$. Oil; boiling-point, 217 218°; $d^{20} = 0.898$.

Alcohol ...... $p = 6.81$, $d^{18} = 0.7985$, $[\alpha]_D^{18} = +43.31°$ [1]

l-FENCHONE. From thuja oil. Crystals, melting-p 5°, boiling-point, 192° to 194°; $d^{20} = 0.948$.

Alcohol .... $p = 14.36$, $d^{23} = 0.815$, $[\alpha]_D^{23} = -66.94°$ [2]

Derivatives: *Oxime*. Resembles closely the *d*-fencl oxime, and in equivalent concentration rotates as strongl the left as the latter does to the right.[2]

d-CARONE (from *d*-carvone, $[\alpha]_D = +62°$), $C_{10}H_{16}O$. I ing-point, 210°, with decomposition; $d = 0.9567$.

$[\alpha]_D = -173.8°$ [3]

MATICO CAMPHOR, $C_{12}H_{20}O$. In matico oil (*Piper ang folium*). Hexagonal crystals. Melting-point, 94°.

Fused .... $d_4^{108} = 0.924$, $[\alpha]_D^{108} = -28.4$

Dissolved in chloroform ... $p = 10$ $d_4^{15} = 1.557$, $[\alpha]_D^{15} = -28.7$

See further, §7

PATCHOULI CAMPHOR, $C_{15}H_{26}O$ In patchouli oil (*Po temon Patchouli*). Hexagonal prisms, melting-point, 54 55°, boiling-point, 206°, $d^{4} = 1.051$. Fused, *t* above $[\alpha] = -118°$

Alcohol .... $[\alpha]_D = -124.5 - 0.21c$ [5]

See further, §7.

D POLYTERPENES

1 *Sesquiterpenes*, $C_{15}H_{24}$

CADINENE (true sesquiterpene). Found in many ethe oils Liquid boiling-point, 274° to 275°; $d^{20} = 0.918$.

Chloroform .... $p = 13.05$, $d^{9.5} = 1.385$, $[\alpha]_D^{9.5} = -98.56°$

Dihydrochloride, $C_{15}H_{24}.2HCl$. Rhombohedral-hemihec prisms Melting-point, 118°.

Chloroform . . $p = 7.212$, $d^{9.5} = 1.460$, $[\alpha]_D^{9.5} = -36.82°$

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[1] Wallach [illegible]

[2] Wallach Ann Chem Liebig, **272**, 102

Baeyer Bruhl Ber d chem Ges **28**, 639

[4] H Traube Ztschr f Kryst **22**, 47

[5] Montgolfier Bull soc. chim [2] **28**, 414

Dihydrobromide, $C_{15}H_{24}.2HBr$. Needles; melting-point, 124°.

Chloroform. . . $p = 7.227$, $d^{9.5} = 1.490$, $[\alpha]_D^{9.5} = -36.13°$

Dihydroiodide, $C_{15}H_{24}.2HI$. Needles; melting-point, 105° to 106°.

Chloroform. . . . $p = 5.568$, $d^{9.5} = 1.507$, $[\alpha]_D^{9.5} = -48°$[1]

α-PARACOTOL. Is probably a hydrate of cadinene, $C_{15}H_{26}O$. Boiling-point, 220° to 222°.

$d^{15} = 0.9262$, $[\alpha]_D = -11.87°$[2]

HEMP OIL. From *Cannabis sativa*. Boiling-point, 120° to 121° (9 mm).

$[\alpha]_D = -10.81°$[3]

PATCHOULENE. From patchouli camphor. Liquid; boiling-point, 254° to 256°.

$d^{13.5} = 0.937$, $[\alpha]_D = -42.1°$[4]

2. *Diterpenes*, $C_{20}H_{32}$.

l-DITERPILENE. From left turpentine oil.

$d^{0} = 0.9446$, $[\alpha]_D = -14.25°$[5]

3. *Triterpene*, $C_{30}H_{48}$.

d-*α*-AMYRILENE. From *α*-amyrin. Crystals, melting-point, 134° to 135°.

Benzene . . . . . . $c = 4$, $[\alpha]_D = +109.48°$[6]

Derivatives. *α-Amyrin*, $C_{30}H_{49}OH$. Fine needles, melting-point, 181° to 181.5°.

Benzene. . . . . $c = 3.839$, $[\alpha]_D^{16.7} = +91.59°$[7]

Oxy-α-amyrin, $C_{30}H_{47}O.OH + 2H_2O$. Needles, melting-point, 207° to 208°.

Benzene . . . . . $c = 1.653$ (anhydrous), $[\alpha]_D^{15.5} = +108.6°$[8]

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[1] Wallach, Conrady Ann Chem (Liebig), **252**, 150

[2] Jobst, Hesse *Ibid*, **199**, 75

[3] Valente Gazz chim ital, **11**, 196

[4] Montgolfier Bull soc chim, **28**, 415

[5] Lafont Compt rend, **106**, 140

[6] Vesterberg, Backstrom Ber d chem. Ges, **20**, 1245

[7] Vesterberg, Svensson *Ibid*, **23**, 3186

[8] Vesterberg, Svensson *Loc cit*

Brom-α-amyrin, $C_{30}H_{48}Br.OH$. Crystals; melting-poi 177° to 178°.

Benzene …… $c = 2.590$, $[\alpha]_D^{16.3} = +72.8°$ [1]

α-Amyrin Acetate, $C_{30}H_{49}.C_2H_3O_2$. Plates, melting-poi 221°.

Benzene …… $c = 4.074$, $[\alpha]_D^{17.6} = +77.0°$ [1]

l-α-AMYRILENE. From the *d*-compound and P_2O_5. Pr matic crystals; melting-point, 193° to 194°.

Benzene ….. $c = 0.8709$, $[\alpha]_D = -104.9°$ [2]

β-AMYRILENE. From *β*-amyrin. Crystals; melting-poi 175° to 178°.

Benzene …… $c = 1.515$, $[\alpha]_D = +112.19°$ [3]
" …… $c = 0.8$ $[\alpha]_D = +110.42$

Derivatives. *β-Amyrin*, $C_{30}H_{49}OH$. Crystals; meltin point, 193° to 194°.

Benzene …… $c = 1.9055$, $[\alpha]_D^{19} = +99.81°$ [1]
" …… $c = 5$ $[\alpha]_D^{15} = +94.2$ [4]

β-Amyrin Acetate, $C_{30}H_{49}.C_2H_3O_2$ Prisms; melting-poi 236°.

Benzene …… $c = 4.151$, $[\alpha]_D^{16.7} = +78.6°$ [1]

β-Amyrin Palmitate, $C_{46}H_{80}O_2$. In coca wax. Crystal, melting-point, 75°.

Benzene …… $c = 2$, $[\alpha]_D^{15} = +54.5°$ [4]

24. Ethereal Oils

The rotation of the active ethereal oils varies in genera more or less, according to the part of the plant from whic they are obtained and the method of preparation (pressure distillation). Besides this, oils of known purity, in mar cases, have not been obtainable in quantity through a suf ciently long period to permit the determination of certain dat

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[1] Vesterberg, Svensson

[2] Vesterberg, Koch Ber. d chem Ges., **24**, 3834

[3] Vesterberg, Backstrom *Ibid*, **20**, 1246

[4] Hesse. Ann Chem (Liebig), **271**, 216

But for a number of oils of the *aurantium* group, on the other hand, it has been possible in the laboratory of Schimmel & Co., of Leipzig, to establish, after years of investigation, the limiting values for the rotation, so that oils which give results outside these may, with considerable certainty, be looked upon as adulterated.

In what follows the data furnished by the reports of this firm will be given, the rotations, α_D, stated are the angles read off directly in degrees and minutes, with a tube length of 100 mm. and sodium light.

Oil of Bergamot (*Citrus bergamia*) $d_{15}^{15} = 0.883$ to 0.886, not below 0.881 $\alpha_D = +9°$ to $+15°$, not above $+20°$ (principal constituents—limonene, dipentene, linalool about 38 per cent, linalyl acetate).

Oil of Lemon (*Citrus limonum*). $d_{15}^{15} = 0.858$ to 0.861. $\alpha_D^{20} = 59°$ to $67°$, not below $59°$. For observations made at temperatures below 20°, under the same conditions, 9′ must be subtracted for each degree C, and for observations made at temperatures above 20°, 8.2′ must be added for each degree. This correction holds for the interval, 10° to 30° C. The rotation does not change on long keeping, even under unfavorable conditions (principal constituents—limonene, citral, no pinene).

Oil of Orange

a *Sweet* (*Citrus aurantium*) $d_{15}^{15} = 0.848$ to 0.852 $\alpha_D^{20} = +96°$ to $98°$, not below $96°$. Temperature correction for 10° to 30° C. for each degree under 20°, $-14.5'$, above 20°, $+13.2'$ (principal constituents—limonene, citral).

b *Bitter* (*Citrus bigaradia*). $d_{15}^{15} = 0.848$ to 0.852 $\alpha_D^{20} = +92°$ to $98°$, not below $92°$ (limonene).

For most of the other oils the limits of rotation have not yet been established with the same certainty. The data in the following list, which likewise have been taken from the Schimmel reports up to April, 1897, may, nevertheless, be found useful for comparison in some cases. For each oil, the first figures refer to the specific gravity at 15°, and the second give the mean rotation for the *D* line in a 100 mm. tube, as read off directly.

Andropogon Oil (*Andropogon laniger*). 0.915 to 0.919, − 4° to + 34°38′. *Andropogon odoratus*, 0.945 to 0.95 − 22° to − 23° (phellandrene).

Angelica Oil (*Archangelica officinalis*). *a.* Fruit: 0.856 to 0.89, + 11° to + 12°. *b.* Fresh plant. 0.869 to 0.886, + 8° to + 21°. *c.* Root: 0.855 to 0.905, + 25° to + 32° (phellandrene, methylethylacetic acid).

Anise Oil (*Pimpinella anisum*). 0.980 to 0.990 Slightly left-rotating, α_D to − 1°50′ (anethol, methyl chavicol, aniseketone).

Asafetida Oil (*Ferula asafetida*). 0.975 to 0.990. $\alpha_D =$ − 9°15′ (pinene? bodies containing sulphur, and compounds $(C_{10}H_{16}O)_n$).

Basilicum Oil (*Ocimum basilicum*). 0.909 to 0.990. $\alpha_D =$ − 22° to + 16° (pinene, cineol, camphor, linalool, methyl chavicol).

Betel Oil (*Piper betle*). Java. 0.958 to 1.04. $\alpha_D =$ + 2°53′ (betelphenol, cadinene, chavicol).

Cajiput Oil (*Melaleuca*, spec.) 0.92 to 0.93 according to province. $\alpha_D =$ − 0°10′ to − 2° (cineol, terpineol, terpenyl acetate).

Calamus Oil (*Acorus calamus*). Fresh roots 0.960 to 0.970. $\alpha_D =$ 20° to 31°. Dry roots: 0.960 to 0.970. $\alpha_D =$ 13° to 21°. Commercial oil: 0.962 to 0.970. α_D never below + 10°.

Camphor-Leaf Oil (*Camphora officinalis*). 0.932. $\alpha_D =$ 4°52′ (camphor).

Caraway Oil (*Carum carvi*). 0.905 to 0.915. $\alpha_D =$ + 70° to + 85° (limonene, carvone).

Cardamom Oil (*Elettaria cardamomum*). Ceylon. 0.895 to 0.910. $\alpha_D =$ + 12° to + 13° (terpenine, dipentene? terpineol?).

Cascarilla Oil (*Croton eluteria*). 0.890 to 0.930. $\alpha_D =$ + 5°.

Cedar-Leaf Oil (*Juniperus virginiana*). 0.884 to 0.886. $\alpha_D =$ + 59.5°.

Cedar-Wood Oil (*Juniperus virginiana*). 0.940 to 0.960.

α_D = − 30° to − 40° (cedrene, cedar camphor). **Oils of different countries and unknown botanical origin, 0.906 to 0.928. α_D = − 5° to − 18° 6′ (cadinene, cedar camphor).**

Celery Oil (Apium graveolens). **Fresh leaves, 0.848 to 0.850.** α_D = − 48° to − 52°. Seed: 0.870 to 0.895. α_D = + 67° to + 79° (limonene).

Conifer Oils:

Turpentine Oil (Pinus spec.): 0.855 to 0.876. American oil, right- and left-rotating. French oil, left-rotating; other European oils are right-rotating (pinene, dipentene in Russian and Swedish oils, also sylvestrene).

Pine Needle Oil (Pinus silvestris). Swedish, 0.872. α_D − 10° 40′. German, 0.884 to 0.886. α_D = − 7° to − 10° (pinene, sylvestrene, bornyl acetate, cadinene). Scottish, 0.885 to 0.889. α_D = − 7° 45′ to − 19°.

Pine Needle Oil (Picea vulgaris). 0.888. α = − 21° 40′ (pinene, phellandrene, dipentene, bornyl acetate, cadinene); from two-year cones, 0.892. α 20° 12′.

Dwarf Pine Oil (Latschenkiefer) (*Pinus pumilio*). 0.865 to 0.875. α_D = − 5° to − 9° (pinene, phellandrene, sylvestrene, 4 to 7 per cent. of bornyl acetate, sesquiterpene).

Silver Fir Oil (Edeltannen) (*Abies pectinata*). Needles, 0.865 to 0.875. α_D = − 20° to − 60° (pinene, limonene, 4.5 to 7 per cent. of bornyl acetate, sesquiterpene). Young cones, 0.855 to 0.870. α_D = − 60° to − 80° (pinene, limonene, 0.5 to 3 per cent. of ester, $C_{10}H_{17}OCH_3CO$).

Hemlock Oil (Abies canadensis). 0.907. α = − 20° to − 26° (pinene, camphene, bornyl acetate, sesquiterpene).

Fir Needle Oil, Siberian (*Abies siberica*). 0.91 to 0.92. α_D = − 40° to − 45° (bornyl acetate).

Coriander Oil (Coriandrum sativum). 0.87 to 0.88. α = + 8° to + 13° (pinene, linalool).

Creeping Thyme Oil (Thymus serpyllium). 0.905 to 0.930. α_D = − 1° to − 11° (thymol, carvacrol, cymol).

Curled Mint Oil (Mentha crispa). 0.92 to 0.98. α_D = − 43° or lower (carvone).

Dill Oil (*Anethum graveolens*). German, Russian, Roumanian fruit: 0.895 to 0.915 $\alpha_D = +70^\circ$ to $+80^\circ$ (limonene, carvone). East Indian fruit: $\alpha_D = +40^\circ$

Dog Fennel Oil (*Eupatorium foeniculaceum*). 0.935. $\alpha_D = +17^\circ 50'$ (phellandrene).

Elemi Oil (*Canarium* spec.). 0.87 to 0.91 $\alpha_D = +45^\circ$ (phellandrene dipentene)

Eucalyptus Oil (*Eucalyptus*, spec.). 0.86 to 0.95 $\alpha_D = -71^\circ$ to $+20^\circ$ according to source (citronellal, cineol, citronellone, pinene, phellandrene, alcohols, and aldehydes of the fatty series).

Fennel Oil (*Foeniculum vulgare* and varieties). 0.920 to 0.987 $\alpha_D = +7^\circ$ to $+22^\circ$ French, to $+48^\circ$ (pinene, phellandrene, dipentene, limonene, fenchone, anethol).

Frankincense Oil (*Boswellea*, spec.). 0.875 to 0.885 $\alpha_D = -11^\circ 35'$ (pinene, phellandrene, dipentene)

Galbanum Oil (*Peucedanum galbaniflunm* and varieties) 0.91 to 0.94. $\alpha_D = -5^\circ$ to $+20^\circ$ (pinene, cadinene)

Geranium Oil (*Pelargonium*, spec.). According to origin 0.886 to 0.906. $\alpha_D = -7^\circ$ to -16° (geraniol, citronellol, and 19 to 33 per cent. of tiglic acid esters of the latter).

Ginger Oil (*Zingiber officinale*) 0.875 to 0.885. $\alpha_D = -26^\circ$ to -44° (camphene, phellandrene)

Gurjon Balsam Oil (*Dipterocarpus*, spec.). 0.92 to 0.93 $\alpha_D = -35^\circ$ to -106°.

Hop Oil (*Humulus lupulus*). 0.855 to 0.88. $\alpha_D = +4^\circ 40'$ and lower (terpenes, humulene)

Juniper Oil (*Juniperus communis*) 0.865 to 0.885. $\alpha_D = \pm 0$ to -18° (pinene, cadinene, juniper camphor).

Lavender Oil (*Lavendula vera*). French. 0.885 to 0.895 $\alpha_D = -3^\circ$ to -9° (linalool, linalyl acetate 30 to 45 per cent., geraniol, cineol). English: 0.885 to 0.900. $\alpha_D = -7^\circ$ to -10° (much cineol, linalyl acetate 7 to 10 per cent.)

Lime Oil, Italian (*Citrus limetta*) 0.872. $\alpha_D = 58^\circ 15'$.

West Indian (*Citrus medica*, var. *acida*). 0.880 to 0.885 $\alpha_D = + 35°$ to $+ 40°$ (limonene, citral).

Mace Oil (*Myristica officinalis*). 0.91 to 0.93 $\alpha_D = + 10°$ (pinene, myristicene).

Mandarin Oil (*Citrus madurensis*) 0.854 to 0.858 $\alpha_D = + 65°$ to $+ 75°$ (citral, limonene).

Mastic Oil (*Pistacia lentiscus*). 0.855 to 0.870 $\alpha_D = + 22°$ to $+ 72°$.

Onion Oil (*Allium cepa*) 1.040. $\alpha_D = - 5°$ ($C_6H_{12}S_2$)

Orange-Flower Oil, sweet (*Citrus aurantium*). 0.87 to 0.890 $\alpha_D = + 16°$ to $+ 29°$. Bitter, *Citrus bigaradia*, 0.87 to 0.885 $\alpha_D = + 5°$ to $+ 10°$ (limonene, linalool, linalyl acetate).

Palma Rosa Oil (*Andropogon Schoenanthus*) 0.888 to 0.896. $\alpha_D = - 1°40'$ to $+ 1°45'$ (dipentine, geraniol, geranyl esters).

Pennyroyal Oil (*Mentha pulegium*, *Hedeoma pulegioides*) 0.93 to 0.96 $\alpha_D = + 17°$ to $+ 23°$ (pulegone)

Peppermint Oil (*Mentha piperita*) German 0.902 to 0.915. $\alpha_D = - 25°$ to $- 32°$ English 0.900 to 0.910 $\alpha_D = - 22°$ to $- 31°$ American 0.910 to 0.920 $\alpha_D = - 25°$ to $- 33°$. Japanese 0.895 to 0.905 $\alpha_D = - 26°$ to $- 42°$ (menthol, menthone, menthol esters of acetic and isovaleric acids, aldehydes, terpenes)

Rosemary Oil (*Rosmarinus officinalis*) Specific gravity not below 0.900. $\alpha_D = + 1°30'$ to $11°$ for French, and $+ 0° 45'$ to $4° 30'$ for Italian (pinene, cineol, borneol, camphor)

Sandalwood Oil (*Santalum*, spec.) East Indian 0.975 to 0.980 $\alpha_D = - 17°$ to $- 20°$. West Indian· 0.963 to 0.967. α_D about $+ 26°$. Australian· 0.953 $\alpha_D = 5° 20'$ (santalol).

Sassafras Oil (*Sassafras officinalis*). Leaves 0.872 $\alpha_D = - 6° 25'$ Bark: 1.065 to 1.095 $\alpha_D = + 1°$ to $+ 4°$ (pinene, phellandrene, safrol, eugenol, camphor).

Savin Oil (*Juniperus Sabina*). 0.910 to 0.925. $\alpha_D = + 45°$ to $+ 60°$ (pinene, cadinene).

Spike Oil (*Lavendula spica*). 0.905 to 0.915. α_D usually to + 3°, seldom to + 7° (pinene, cineol, linalool, camphor, borneol, terpineol (?), geraniol (?)).

Star Anise Oil (*Illicium verum*). 0.98 to 0.99. $\alpha_D = +$ 0° 40′ to — 2° (pinene, phellandrene, methyl chavicol, anethol).

Storax Oil (*Liquidambar orientalis*). 0.89 to 1.06. $\alpha_D =$ — 15° (styrol, cinnamic acid esters).

Sweet Marjoram Oil (*Origanum majorana*). 0.89 to 0.91. $\alpha_D = +$ 15° to + 18°.

Tansy Oil (*Tanacetum vulgare*). Fresh plant: 0.915 to 0.930. Dry plant 0.954. $\alpha_D = +$ 30° to 45°. English: $\alpha_D =$ about — 27° (thujone, camphor, borneol)

Thuja Oil (*Thuja occidentalis*). 0.915 to 0.930 $\alpha_D = -$ 6° to — 13° (thujone, fenchone, pinene).

Tarragon Oil (*Estragon Oil*) (*Artemisia dracunculus*). 0.89 to 0.96 $\alpha_D = +$ 2° to + 9° (methyl chavicol)

Valerian Oil (*Valeriana officinalis*) 0.93 to 0.95 $\alpha_D =$ — 8° to — 15° (pinene, camphene, borneol, bornyl esters).

Ylang-Ylang Oil (*Anona odoratissima*). 0.91 to 0.95. $\alpha_D = -$ 20° to — 55° (benzoic acid esters, linalool, geraniol, etc.)

25. Resin Acids

DEXTROPIMARIC ACID, $C_{20}H_{30}O_2$.

Chloroform...... $c = 10.10$, $t = 20°$, $[\alpha]_D = -73.36°$[1]

ABIETINIC ACID, $C_{19}H_{28}O_2$.

$[\alpha]_D = -66.66°$ to $-67.34°$[2]

PODOCARPINIC ACID, $C_{17}H_{22}O_3$.

Alcohol......	$c = 4$ to 9,	$[\alpha]_D = +136°$	[3]
Ether	$c = 4$ to 7,	" $= +130$	

Sodium Salt, $C_{17}H_{21}O_3Na + 8H_2O$.

Water.................	$c = 4.6$,	$[\alpha]_D = 82°$	[4]
"	$c = 6.4$,	" $= 79$	
"	$c = 13.8$,	" $= 73$	
Alcohol	$c = 9.0$,	" $= 86$	

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[1] Rimbach Ber d pharm Ges, (1896), p 63

[2] Mach. Monatsh Chem, 15, 627

[3] Oudemans · Ann Chem (Liebig), 166, 65

[4] Oudemans *Loc cit*

TURPETHINIC ACID, $C_{34}H_{60}O_{18}$. Melting-point, 168°.
$[\alpha]_D = -37.49°$

CONVOLVULINIC ACID. Melting-point, 175°.
$[\alpha]_D = -45.30$[1]

26. Alkaloids

Alkaloids of the Aconite Species

ACONITINE, $C_{33}H_{45}NO_{12}$. Rhombic crystals; melting-point, 188.5° (corr.)

Alcohol.. ... $p = 3.726$, $[\alpha]^{23}_D = -11.01°$ }[2]
" ...... $c = 2.746$, $[\alpha]^{20}_D = +11.10$ }

Formerly described as left-rotating. See Jürgens.[3]

Hydrobromide, $C_{33}H_{45}NO_{12}.HBr + 2^1/_2H_2O$. Crystals.

Water....... .. .... $c = 5.183$, $[\alpha]^{20}_D = -31.3°$ }[4]
Recrystallized ..... . $p = 1.95$, " $= -30.47$ }

ISACONITINE (Napelline), $C_{33}H_{45}NO_{12}$. Crystals; melting-point, 125° (corr.).

Alcohol . ... $c = 7.86$, $[\alpha]^{15}_D = -4.48°$

Hydrochloride, $C_{33}H_{45}NO_{12}$ HCl + H_2O White needles; melting-point, 268° (corr.)

Water.. .... $c = 1$, $[\alpha]^{15}_D = -28.74°$

Hydrobromide, $C_{33}H_{45}NO_{12}.HBr$. Needles; melting-point, 282° (corr.)

Water....... .... $c = 1$, $[\alpha]^{15}_D = -30.47°$

Hydroiodide, $C_{33}H_{45}NO_{12}$ HI Crystals; melting-point, 242° (corr).

Water........ ... $c = 1$, $[\alpha]^{15}_D = -26.94°$[5]

PYROACONITINE, $C_{31}H_{41}NO_{10}$.

Water... ...... $c = 1.121$, $[\alpha]^{15}_D = -90.99°$

Hydrobromide, $C_{31}H_{41}NO_{10}.HBr$.

Water .... $c = 2.136$, $[\alpha]^{15}_D = -46.8°$

PYROACONINE, *Hydrochloride*, $C_{24}H_{37}NO_9.HCl + H_2O$.

Water... ..... $c = 1.96$, $[\alpha]^{15}_D = -102.07°$[6]

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[1] Kromer Z Oesterr Apothek.-V, **49**, 520
[2] Dunstan, Ince J. Chem. Soc, **59**, 281
[3] Jahresb, 1885, 1722
[4] Dunstan, Ince *Loc cit*
[5] Dunstan, Harrison J Chem Soc, **63**, 445.
[6] Dunstan, Carr *Ibid*, **65**, 176

ACONINE, $C_{26}H_{41}NO_{11}$. Amorphous: melting-point, 132° (corr.). By hydrolysis from isaconitine.

Water .... $p = 3.534$, $d_4^{15} = 1.01$ $[\alpha]_D^{15} = -23°$

Hydrochloride, $C_{26}H_{41}NO_{11}.HCl + 2H_2O$. Crystals, melting-point, 175.5° (corr.)

Water, $p = 5.75$ (anhydrous), $d_4^{15} = 1.015$, $[\alpha]_D^{15} = -7.71°$[1]
Water, $c = 2.398$ (anhydrous), $[\alpha]_D^{15} = -7.72°$[2]

LYCACONITINE, $C_{27}H_{41}N_2O_6 + 2H_2O$ Amorphous; melting-point, 111.7° to 114.8°.

Alcohol.......... $p = 10$, $[\alpha]_D = -31.5°$[3]

ATISINE, $C_{22}H_{31}NO_2$ (from *Aconitum heterophyllum*):
Alcohol .... $[\alpha]_D = -19.6°$

Hydrochloride $(C_{22}H_{31}NO_2)HCl$, m p 296° Water, $[\alpha]_D = -18.46°$ }[4]
Hydrobromide " " HBr, " 273° " " $= +24.3$ }
Hydroiodide " " HI, " 279°-280° " " $= +27.4$ }

For later observations on aconite alkaloids, see Dunstan and Carr,[5] and Dunstan and Read.[6]

ARGININE, $C_6H_{14}N_4O_2$ The free base has not been investigated.

Hydrochloride, $C_6H_{14}N_4O_2.HCl$. Monoclinic crystals.

Water. .... $c = 8$, $[\alpha]_D = -33.1°$[7]

Nitrate, $C_6H_{14}N_4O_2.HNO_3 + \frac{1}{2}H_2O$. Needles.

Water.......... . $c = 10$, $[\alpha]_D^{17} = -28.75°$[7]

ARIBINE, $C_{23}H_{20}N_4 - 8H_2O$. Crystals: melting-point, 229°. Inactive[8]

ASPIDOSPERMINE, $C_{22}H_{30}N_2O_2$ Prismatic crystals, melting-point, 205° to 206°.

Alcohol (97 vol p. c.)...... $c = 2$, $[\alpha]_D^{15} = -100.2°$ }[9]
Chloroform.... .... $c = 2$, " $= -83.6$ }
Water — 3 mol. HCl...... $c = 2$, " $= -61.6$ }
" — 10 " " ...... $c = 2$, " $= -62.2$ }

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[1] Dunstan Passmore J Chem Soc 61, 400
[2] Dunstan Harrison *Loc cit*
[3] Dragendorff, Spohn Ber d chem Ges, 17, Ref 375
[4] Jowett Chem News 74, 120
[5] J Chem Soc 71, 350.
[6] *Ibid* 77, 45.
[7] Schulze, Steiger Ztschr phys Chem, 11, 43
[8] Rieth Inaug-Diss, Göttingen, 1861
[9] Hesse Ann Chem (Liebig), 211, 254.

ASPIDOSPERMATINE, $C_{22}H_{28}N_2O_2$. Wart-like lumps; melting-point, 162°.

Alcohol (97 vol p. c.).......... $c = 2$, $[\alpha]_D^{15} = -72.3°$[1]

QUEBRACHINE, $C_{21}H_{26}N_2O_3$. Prisms; melting-point, 214° to 216° (uncorr.).[2]

Alcohol (97 vol. p. c.).... $c = 2$, $[\alpha]_D^{15} = -62.5°$ }[3]

Chloroform.............. $c = 2$, " $= -18.6$ }

PAYTINE, $C_{21}H_{24}N_2O + H_2O$. Crystals; melting-point, 156°.

Alcohol (96 (?) vol p. c.)....... $c = 0.454$, $[\alpha]_D^{15} = -49.5°$[4]

ATROPINE, $C_{17}H_{23}NO_3$. Crystals; melting-point, 115° to 116°.

Absolute alcohol.. $c = 3.22$, $[\alpha]_D^{15} = -0.4°$[5]

Alcohol.......... $c = 6.67$, $[\alpha]_D^{20} = -1.89°$[6]

According to Ladenburg[7] and Gadamer[8] atropine is optically inactive

The *Atropinum naturale* is a mixture of atropine and hyoscyamine.

Sulphate, $(C_{17}H_{23}NO_3)_2H_2SO_4 + H_2O$. Crystals.

Water...... $c = 2$ (anhydrous), $[\alpha]_D^{15} = -8.8°$[9]

SCOPOLAMINE, $C_{17}H_{21}NO_4 + H_2O$. Melting-point, 59°

Absolute alcohol.... $p = 2.65$, $[\alpha]_D = -13.7°$[10]

Melting-point, 56°.

Water. ...... $[\alpha]_D = -14.97°$[11]

HYOSCYAMINE, $C_{17}H_{23}NO_3$. White needles melting-point, 108° to 109°.

Absolute alcohol......... $c = 17.2$, $[\alpha]_D = -21.60°$ }

" " .... $c = 12.4$, " $= -21.76$ }[12]

" " ...... $c = 6.2$, " $= -21.25$ }

" " .... $c = 3.1$, " $= -20.26$ }

Alcohol (50 per cent).... $c = 12.4$, " $= -20.27$

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[1] Hesse Loc cit 259

[2] Hesse Ber d chem Ges, 13, 2308

[3] Hesse Ann Chem (Liebig), 211, 265

[4] Hesse *Ibid*, 166, 272

[5] Hesse *Ibid*, 271, 101

[6] Will, Bredig Ber d chem Ges, 21, 2777

[7] Ber d chem Ges, 21, 3065

[8] Arch Pharm, 234, 543

[9] Hesse *Loc cit.*

[10] Hesse. Ann Chem. (Liebig), 271, 111

[11] Zuboldt Diss., Marburg, 1895.

[12] Will. Ber d chem. Ges, 21, 1717

Alcohol....... $c = 1$ to 12, $[\alpha]_D^{20} = -21.016 - 0.0154\,c$ [1]
Absolute alcohol. $c = 3.22$, $[\alpha]_D^{15} = -20.3°$ [2]

By action of bases, hyoscyamine is converted into atropine.[3]

Sulphate, $(C_{17}H_{23}NO_3)_2H_2SO_4 + 2H_2O$. White needles; melting-point, 201°.

Water....... ..... $c = 2$ (anhydrous), $[\alpha]_D^{15} = -28.6°$ [4]
Water...... ...... $p = 2.9$, $[\alpha]_D = -26.8$ to $-27.3°$ [5]

Oxalate, anhydrous.

Water .... $p = 1.6$, $[\alpha]_D = -24.07°$ [6]

PSEUDOHYOSCYAMINE, $C_{17}H_{23}NO_3$. Yellow needles; melting-point, 133° to 134°.

Absolute alcohol... $p = 5.26$, $[\alpha]_D = -21.15°$ [7]

HYOSCINE, $C_{17}H_{21}NO_4$(?). Hard, transparent, resin-like masses; melting-point, 55°.

Absolute alcohol . . $c = 2.65$, $[\alpha]_D^{15} = -13.7°$ [8]

The rotation is greatly decreased by addition of a small amount of sodium hydroxide solution.

Hydrobromide, $C_{17}H_{21}NO_4.HBr + 3H_2O$ Rhombic crystals.

Water .... $c = 4$, $[\alpha]_D^{15} = -22.5°$ [4]

BEBIRINE, $C_{18}H_{21}NO_3$. Melting-point, 214°.

Absolute alcohol ...... $p = 1.6$, $[\alpha]_D^{28} = -298°$ [9]

BERBERINE, $C_{20}H_{17}NO_4 + 4H_2O$ Crystals, melting-point, 120°. Inactive

OXYACANTHIN, $C_{18}H_{19}NO_3$. Crystals; melting-point, 138° to 150° (from water); 208° to 214° (from alcohol).

1 vol. alcohol (97 vol. p c) — 2 vol chloroform, $c = 4$, $[\alpha]_D^{15} = +131.6°$ [10]

Hydrochloride $C_{18}H_{19}NO_3.HCl + 2H_2O$ Needles

Water .... $c = 2$, $[\alpha]_D^{15} = +163.6°$ [4]

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[1] Hammerschmidt, Will and Bredig Ber d chem Ges, **21**, 2784
[2] Hesse Ann Chem (Liebig), **271**, 103
[3] Will and Bredig Ber d chem. Ges, **21**, 2777
[4] Hesse *Loc cit*
[5] Gadamer Arch Pharm, **234**, 543.
[6] Gadamer *Loc cit*
[7] Merck Arch Pharm, **231**, 117
[8] Hesse Ann Chem (Liebig), **271**, 110
[9] Scholtz Ber d chem Ges, **29**, 2058
[10] Hesse *Ibid*, **19**, 3192

HYDRASTINE, $C_{21}H_{21}NO_6$. Rhombic crystals; melting-point, 132°.

Chloroform …………	$c = 2.552$,	$[\alpha]_D^{17} = -67.8°$	[1]
Water + 2 mol. HCl..	$c = 4.050$,	" $= -127.3$	
Chloroform ……. ..	$c = 3.042$,	$[\alpha]_D = -57.5°$	[2]

Methylhydrastine Hydrochloride, $C_{22}H_{23}NO_6.HCl$. Crystals; melting-point, 241°. Inactive in aqueous solution.[3]

HYDRASTININE, $C_{11}H_{11}NO_2 + H_2O$. Crystals, melting-point, 116° to 117° Inactive in aqueous solution.[4]

CHELERYTHRINE (Sanguinarine), $C_{17}H_{15}NO_4$. Crystals, melting-point, 160°. Inactive.

Cinchona Alkaloids[5]

CUPREINE, $C_{19}H_{22}N_2O_2 + 2H_2O$ Prisms; melting-point, 197° to 198° The following determinations on the alkaloid and its salts were made by Oudemans.[6]

Absolute alcohol…	$c =$	0.69,	1.24,	1.78°
" " .	$[\alpha]_D^{17} =$	-175.4,	-175.5,	$-173.3°$
Alcohol (97 p c) .	$c =$	1.50,	$[\alpha]_D^{16} = -175.3°$	

Neutral Hydrochloride, $C_{19}H_{22}N_2O_2.HCl + H_2O$ Colorless needles.

Water . ..	$c = 0.567$,	$[\alpha]_D^{17} = -157.1°$,	alcohol,	$[\alpha]_D^{17} = -184.7°$
" . …… .	$c = 0.871$,	" $= -154.8$,	"	" $= -182.0$
Absolute alcohol	$c = 0.927$,	" $= -169.7$,	"	" $= -199.8$
" " ..	$c = 1.421$,	" $= -167.3$,	"	" $= -196.7$

Acid Hydrochloride, $C_{19}H_{22}N_2O_2.2HCl$ Hard crystals, $+ 2H_2O$, rhombic crystals

Water,	$c = 1.194$ (hydrated),	$[\alpha]_D^{17} = -211.0°$,	alkaloid,	$[\alpha]_D^{17} = -283.8°$
"	$c = 2.508$	" " $= -210.6$,	"	" $= -282.3$
"	$c = 4.687$	" " $= -206.0$,	"	" $= -276.2$
"	$c = 8.589$	" " $= -200.4$,	"	" $= -268.6$
"	$c = 17.278$	" " $= -191.1$,	"	" $= -256.2$

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[1] Freund, Will Ber d chem. Ges, **19**, 2797

[2] Eijkman Rec trav chim Pays-Bas, **5**, 290

[3] Freund and Rosenberg Ber d. chem Ges, **23**, 404

[4] Freund, Will *Loc cit*

[5] Numerous earlier observations on the rotation of the alkaloids were made by Bouchardat: Ann chim phys, [3], **9**, 213. Bouchardat and Boudet J pharm Chim, [3], **23**, 288; Buignet: *Ibid*, [3], **40**, 268, DeVrij and Alluard Compt. rend, **59**, 201 The numerical data refer to Biot's red ray, but they cannot be used, as the nature of the solvent and the concentration are, in most cases, not given.

[6] Rec. trav chim Pays-Bas, **8**, 153

Water, + 5 26 cc. norm. HCl $c =$ 2.088 (hydrated), $[\alpha]_D^{17} = -$ 210 8°
alkaloid, " $= -$ 282 6
" + 10 53 cc norm HCl $c =$ 2.070 (hydrated), " $= -$ 210.2
alkaloid, " $= -$ 281.7
" + 22 73 cc. norm. HCl $c =$ 21 987 (hydrated), " $= -$ 205.5
alkaloid, " $= -$ 276.4
" + 52 63 cc norm. HCl $c =$ 2 085 (hydrated), " $= -$ 199 5
alkaloid, " $= -$ 267.8
" + 90 90 cc. norm HCl $c =$ 2.056 (hydrated), " $= -$ 194.0
alkaloid, " $= -$ 260 9

Neutral Hydrobromide, $C_{19}H_{22}N_2O_2$ HBr + H_2O. White needles.

Water........ $c =$ 0.491, $[\alpha]_D^{17} = -$ 145 8°, alkaloid, $[\alpha]_D^{17} = -$ 192 7°
" ...... $c =$ 1.180, " $= -$ 144 8, " " $= -$ 191 1
Absol alcohol $c =$ 1 434, " $= -$ 139.2, " " $= -$ 183 7
" " $c =$ 1 687, " $= -$ 137 3, " " $= -$ 181 1

Acid Hydrobromide, $C_{19}H_{22}N_2O_2$.2HBr. Crystals.

Water .... $c =$ 1 564, $[\alpha]_D^{17} = -$ 189 0°; alkaloid, $[\alpha]_D^{17} = -$ 287 7°
" .... $c =$ 2 991, " $= -$ 184 6; " " $= -$ 281 0
" .... $c =$ 7.012, " $= -$ 176 8; " " $= -$ 268 6.

Neutral Hydroiodide, $C_{19}H_{22}N_2O_2$.HI. Crystals.

Water........ $c =$ 0.802, $[\alpha]_D^{17} = -$ 126 3°; alkaloid, $[\alpha]_D^{17} = -$ 178 4°
Absol alcohol $c =$ 0.982, " $= -$ 128 3, " " $= -$ 180.9

Acid Hydroiodide, $C_{19}H_{22}N_2O_2$ 2HI (at 150°) Yellow crystals.

Water........ $c =$ 1 504, $[\alpha]_D^{17} = -$ 151 2°, alkaloid, $[\alpha]_D^{17} = -$ 283 2°
" .... $c =$ 1 491, " $= -$ 147.6; " " $= -$ 276 4

Neutral Nitrate, $C_{19}H_{22}N_2O_2$ $HNO_3 + 2H_2O$. White needles.

Water...... $c =$ 1.129, $[\alpha]_D^{17} = -$ 138 4°, alkaloid, $[\alpha]_D^{17} = -$ 182 5°

Acid Nitrate, $C_{19}H_{22}N_2O_2.2HNO_3 + H_2O$. Light yellow crystals.

Water........ $c =$ 1.283, $[\alpha]_D^{17} = -$ 179 4°; alkaloid, $[\alpha]_D^{17} = -$ 289 1°
" .... $c =$ 2 347, " $= -$ 193.4; " " $= -$ 283.2
" .... $c =$ 3 815, " $= -$ 188.9; " " $= -$ 276.7
" .... $c =$ 5 035, " $= -$ 189 8, " " $= -$ 278.0
" ...... $c =$ 6 551, " $= -$ 188 9; " " $= -$ 276 7

Chlorate, $C_{19}H_{22}N_2O_2.HClO_3$. Fine white needles.

Water........ $c =$ 1.033, $[\alpha]_D^{17} = -$ 144.9°; alkaloid, $[\alpha]_D^{17} = -$ 184.4°

Neutral Sulphate, $C_{19}H_{22}N_2O_2.H_2SO_4 + 2H_2O$. Crystals.

Water[1] .... $c = 0.905$, $[\alpha]_D^{17} = -202\ 4°$, alkaloid, $[\alpha]_D^{17} = -289.9°$
" ..... $c = 1.087$, $[\alpha]_D^{18} = -197\ 1$; " $[\alpha]_D^{18} = -282\ 3$
" .... $c = 1\ 110$, $[\alpha]_D^{19\ 5} = -196\ 7$, " $[\alpha]_D^{19\ 5} = -281.7$
" ..... $c = 1\ 437$, $[\alpha]_D^{18} = -197\ 4$, " $[\alpha]_D^{18} = -282.8$
" ..... $c = 1.563$, $[\alpha]_D^{16} = -200\ 1$, " $[\alpha]_D^{16} = -286.6$
" . . . $c = 1\ 605$, $[\alpha]_D^{17} = -199\ 2$, " $[\alpha]_D^{17} = -285\ 3$
" . . $c = 2\ 130$, $[\alpha]_D^{18} = -197.0$, " $[\alpha]_D^{18} = -282\ 2$
" .... $c = 2.766$, $[\alpha]_D^{17} = -196\ 1$; " $[\alpha]_D^{17} = -280\ 9$

Formate, $C_{19}H_{22}N_2O_2.CH_2O_2$. White needles.

Water, $c = 0\ 4804$, $[\alpha]_D^{17} = -163.8°$, alkaloid, $[\alpha]_D^{17} = -183.0°$ (p 167)

Oudemans has also carried out investigations on the effect of alkalies (KOH, NaOH, LiOH, BaO_2H_2, NH_3) on the specific rotation of cupreine.[2]

QUININE (Methyl ester of cupreine), $C_{19}H_{21}N_2O\ OCH_3 + 3H_2O$. Crystals; melting-point, 172 8°[3]

Ether ($d = 0\ 7296$) . $c = 1\ 5$ to 6, $[\alpha]_D^{15} = -158\ 7 + 1\ 911\ c$ [4]
Alcohol (97 vol p c) $c = 1$ " 10, " $= -145\ 2 + 0\ 657\ c$
Chlorof -alcohol, $c = 2$, $[\alpha]_D^{15} = -141\ 0$; $c = 5$, $[\alpha]_D^{15} = -140\ 5$

Anhydride, $C_{20}H_{24}N_2O_2$. Amorphous

Alcohol (97 vol p. c) $c = 1$, $[\alpha]_D^{15} = -170\ 5°$, $c = 2$, $[\alpha]_D^{15} = -169\ 25°$ [5]
Chloroform .... $c = 2$, " $= -116\ 0°$, $c = 5$, " $= -106\ 6$

The following observations, *a*, *b*, and *c*, were made by Oudemans.[6]

a. Absolute alcohol. Determinations for different concentrations and temperatures ·

t	$c = 1$	$c = 2$	$c = 3$	$c = 4$	$c = 5$	$c = 6$
0°	− 171.4	− 169 6	− 167.9	− 166 1	− 164 2	− 162 4
5	170 5	168 7	167 0	165.2	163 4	161.6
10	169.6	167 8	166.1	164 4	162 7	160 9
15	168.9	167 1	165.4	163 7	162 1	160 4
20	168 2	166 6	164 8	163.2	161.6	159 8

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[1] Oudemans, p 166
[2] Rec trav. chim Pays-Bas, **9**, 171
[3] Grimaux Compt rend., **114**, 672
[4] Hesse Ann Chem (Liebig), **176**, 206
[5] Hesse *Ibid.*, **176**, 208.
[6] *Ibid*, **182**, 44

b. Aqueous alcohol, $c = 1.62$, $t = 17°$

Strength of alcohol in p. c.	100 0	94.9	93.5	90 5	83 3	73 9	65.1
$[\alpha]_D$	— 167 5°	169.7	170 4	171 9	174 3	176 1	176.5°

c.

	Benzene	Toluene	Chloroform	
$c =$	0.61	0 39	0 775	1 465
$[\alpha]_D^{17} =$	— 136	— 127	— 126	— 117°

Chloroform-alcohol mixture.... $p = 0.7$ to 2 3, $[\alpha]_D^{16\ 8-17\ 4} = -164.4°$ [1]

Hydrochloride, $C_{20}H_{24}N_2O_2.HCl + 2H_2O$. Long asbestos-like prisms.

a. Water ...... $c = 1.54$ to 1 62 (calc as alkaloid),
$[\alpha]_D^{17} = -133.7°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -163\ 6°$.
Absolute alcohol $c = 1.54$ to 1.62 (as alkaloid),
$[\alpha]_D^{17} = -138\ 0°$ (anhydrous); alkaloid, $[\alpha]_D^{17} = -169\ 0°$. [2].

The following data, *b* to *e*, are by Hesse [3]

b Water.............. $c = 1$ to 3, $[\alpha]_D^{15} = -144\ 98 + 3.15\,c$,
alkaloid, " $= -167.41 + 4\ 71\,c$,
2 mol HCl + water, $c = 1$ to 7, " $= -229\ 46 + 2.21\,c$,
alkaloid, " $= -280\ 78 + 3\ 31\,c$,
Alcohol (97 vol p c) $c = 1$ to 10,
$[\alpha]_D = -147\ 30 + 1\ 958\,c - 0\ 1039\,c^2 + 0\ 00211\,c^3$

c When aqueous alcohol was used, the specific rotation showed a maximum with 60 volume per cent. of alcohol. For $c = 2$ and $t = 15°$, the following figures were obtained

Alcoholic strength

Vol. p c.	97	90	85	80	70
$[\alpha]_D =$	— 143 86	— 160 75	— 168 25	— 174 75	— 182 27

Alcoholic strength

Vol p c	60	50	40	20	0 (water)
$[\alpha]_D =$	— 187.75	— 187.50	— 182.82	— 166.59	— 138.75°

Chloroform-alcohol mixture, $c = 2$, $[\alpha]_D^{15} = -126.25°$

d. Chloroform. Anhydrous salt, $c = 0.9$ to 9 ·
$[\alpha]_D^{15} = -81.81 + 23\ 756\,c - 3\ 9556\,c^2 + 0\ 2198\,c^3$

e. Dilute hydrochloric acid To 1 mol. of salt, *n* mol. HCl, $c = 2$

n	0	1	2	4	10	16
$[\alpha]_D^{15} =$	— 138 75	— 223 2	— 225 7	— 223 6	— 213 9	— 209.5°

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[1] Lenz Ztschr anal. Chem, **27**, 549
[2] Oudemans Ann Chem (Liebig), **182**, 46.
[3] *Ibid*, **176**, 210

Fuming hydrochloric acid, $c = 2$, $[\alpha]_D^{15} = -158.8°$.

Diquinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$. Crystals.

Alcohol (80 vol. p. c.)......... $c = 2$, $[\alpha]_D^{15} = -162.95°$ [1]
" (60 ")......... $c = 2$, " $= -166.36$
Water + 4 mol. HCl.......... $c = 2$, " $= -239.2$
Chloroform-alcohol mixture... $c = 1$ to 5, " $= -157.5 + 0.27c$
40 cc. normal HCl + water.... $c = 8$ (anhydrous), $[\alpha]_D^{15} = -229.03°$ [2]

$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 7^1/_2\ H_2O$.

Absol. alcohol, $c = 1.54$ to 1.62 (calculated as alkaloid), salt anhydrous, $[\alpha]_D^{17} = -157.4°$; alkaloid $[\alpha]_D^{17} = -214.9°$ [3]
Absol. alcohol, $c = 1.3$, $[\alpha]_D^{17} = -155.2°$, $c = 2.0$, $[\alpha]_D^{17} = -158.4°$ [4]

Quinine Sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4 + 7H_2O$. Rhombic crystals.

Water........ $c = 1$ to 6, salt, $[\alpha]_D^{15} = -164.85 + 0.31c$,
alkaloid, $[\alpha]_D^{15} = -278.71 + 0.89c$
Alcohol (97 vol. p. c.) .... $c = 2$, $[\alpha]_D^{15} = -134.75°$ [5]
" (80 ") ..... $c = 2$, " $= -142.75$
" (60 ")...... $c = 2$, " $= -155.91$
Chloroform-alcohol mixture $c = 2$, " $= -138.75$

Water........ $c = 1.54$ to 1.62 (calc. as alkaloid), [3]
$[\alpha]_D^{17} = -213.7°$ (anhydrous); alkaloid, $[\alpha]_D^{17} = -278.1°$
Absol. alcohol $c = 1.54$ to 1.62 (calc. as alkaloid),
$[\alpha]_D^{17} = -134.5°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -227.6°$

The specific rotation of alcoholic solutions, with $c = 2$, decreases, with elevation of temperature, 0.65 for 1° C.[6]

Quinine Disulphate, $C_{20}H_{24}N_2O_2.2H_2SO_4 + 7H_2O$. Prisms.

Water...................... $c = 2$ to 10, $[\alpha]_D^{15} = -170.3 + 0.94c$ [7]
Alcohol (80 vol. p. c.)....... $c = 1$, " $= -154.5$
" (80 ")....... $c = 3$, $[\alpha]_D^{13} = -153.3°$

$C_{20}H_{24}N_2O_2.2H_2SO_4 + 4H_2O$.

Water ...... $c = 2$ to 10, $[\alpha]_D^{15} = -155.69 + 1.14c$
Alkaloid " $= -284.48 + 3.79c$

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[1] Hesse: Ann. Chem. (Liebig), 176, 213

[2] Hesse. Ibid., 205, 219

[3] Oudemans. Ibid., 182, 46

[4] Oudemans. Rec. trav. chim. Pays-Bas, 1, 27

[5] Hesse. Ann. Chem. (Liebig), 176, 215

[6] Draper. Am. J. Sci., [3], 11, 42.

[7] Hesse. Ann. Chem. (Liebig), 176, 217

1 mol quinine hydrate + 3 mol H_2SO_4 + water to 100 cc., $c = 1$ to 5.

$$[\alpha]_D^{15} \text{ (calc as hydrate)} = -246.63^\circ + 3.08\,c$$
$$[\alpha]_D^{15} \text{ (alkaloid)} = -287.72^\circ + 4.19\,c$$

1 mol. sulphate + 2 mol. H_2SO_4 + water to 100 cc. $c = 1$ to 10

Salt $[\alpha]_D^{15} = -171.68 + 0.78\,c$, alkaloid, $[\alpha]_D^{15} = -290.36^\circ + 2.23\,c$

1 mol. disulphate + 1 mol. H_2SO_4 + water to 100 cc. $c = 2$ to 6.

Disulphate $[\alpha]_D^{15} = -153.87 + 0.92\,c$, alkaloid, $[\alpha]_D^{15} = -281.15^\circ + 3.11\,c$[1]

Oxalate, $(C_{20}H_{24}N_2O_2)_2C_2H_2O_4 + 6H_2O$ Long prisms.

Chloroform-alcohol mixture..... $c = 1$ to 3, $[\alpha]_D^{15} = -141.58 + 0.58\,c$[2]

Salt with 3 Mol Water of Crystallization

Absolute alcohol.......... $c = 1.54$ to 1.62 (calc as alkaloid), $[\alpha]_D^{17} = -131.4^\circ$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -160.5^\circ$[3]

Quinine Sulphonic Acid, $C_{20}H_{23}N_2O_2\,HSO_3 + H_2O$. Prisms; melting-point, 209°

3 mol HCl + water. .. . $c = 2$ (anhydrous) $[\alpha]_D^{15} = -182.2^\circ$[4]

Cupreine Ethyl Ester, $C_{19}H_{21}N_2O\,OC_2H_5$. White amorphous mass, melting-point, 160°

Absolute alcohol.......... $[\alpha]_D = -169.4^\circ$[5]

Cupreine Propylester Sulphate, $(C_{19}H_{21}N_2O.OC_3H_7)_2.H_2SO_4 + 1^1/_2H_2O$ Crystals, melting-point, 223° to 224°.

Concentrated aqueous solution of the salt dried at 100°:

$$[\alpha]_D^{22} = -229.5^\circ$$ [6]

Cupreine Isopropylester Sulphate, $(C_{19}H_{21}N_2O.OC_3H_7)_2.H_2SO_4 + H_2O$. Crystals, melting-point, 154°

Concentrated aqueous solution of the salt dried at 125°

$$[\alpha]_D^{22} = -229.2^\circ$$ [7]

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[1] Hesse Ann Chem. (Liebig), **176**, 182

[2] Hesse. *Ibid*, **176**, 218

[3] Oudemans *Ibid*, **182**, 46

[4] Hesse· *Ibid*, **267**, 141

[5] Grimaux, Arnaud. Compt rend, **112**, 1364

[6] Grimaux and Arnaud *Ibid.*, **114**, 672

[7] Grimaux and Arnaud. *Loc cit*

Cupreine-Quinine (*Homoquinine*), $C_{19}H_{22}N_2O_2.C_{20}H_{24}N_2O_2 + 4H_2O$. Triclinic crystals; melting-point, 177°.

Alcohol .... $c = 5$, $[\alpha]_D = -158°$ [1]

Sulphate, $(C_{19}H_{22}N_2O_2.C_{20}H_{24}N_2O_2)_2.H_2SO_4 + 6H_2O$ Colorless prisms.

40 cc norm. HCl + 60 cc. water, $c = 5$ (anhydrous), $[\alpha]^{15}_D = -235.6°$ [2]
Water with 0.5 p. c. H_2SO_4, $c = 5$, $[\alpha]_D = -209°$ [3]
" " 1.0 " " $c = 5$, " $= -220$

Nitrocamphor Quinine, $C_{20}H_{24}N_2O_2 + 2C_{10}H_{14}(NO_2)O + H_2O$. Needles; melting-point, about 131 (decomposes).

Alcohol .... $p = 2.72$, $[\alpha]_j = +45.9°$ [4]

Acetyl Quinine, $C_{20}H_{23}(C_2H_3O)N_2O_2$. Prisms; melting-point, 108°

Alcohol (97 vol. p. c.)...... $c = 2$, $[\alpha]^{15}_D = -54.3°$ [5]
3 mol. HCl + water........ $c = 2$, " $= -114.8$

Propionyl Quinine, $C_{20}H_{23}(C_3H_5O)N_2O_2$. Rhombic prisms; melting-point, 129°.

3 mol. HCl + water.. .... $c = 2$, $[\alpha]^{15}_D = -108.8°$ [6]

APOQUININE, $C_{19}H_{22}N_2O_2 + 2H_2O$. Amorphous, melting-point, 160° (turns brown)

Alcohol (97 vol. p. c.).. .... $c = 2$ (anhydrous), $[\alpha]^{15}_D = -178.1°$ [7]
3 mol. HCl + water ..... $c = 2$ " " $= -246.6$
Alcohol (97 p. c.).. ... . $c = 0.7877$, $[\alpha]^{15}_D = -217.1°$ [8]

Diacetylapoquinine, $C_{19}H_{20}(C_2H_3O)_2N_2O_2$. Amorphous

Alcohol (97 vol. p.c.). .... $c = 2$, $[\alpha]^{15}_D = -61.8°$ [9]
3 mol. HCl + water....... $c = 2$, " $= -107.5$

Hydrochlorapoquinine,, $C_{19}H_{23}ClN_2O_2 + 2H_2O$. Flakes, melting-point, 160°.

Alcohol (97 vol. p. c.) .. . $c = 2$ (anhydrous), $[\alpha]^{15}_D = -149.1°$ [10]
3 mol. HCl + water .... $c = 2$ " " $= -245.7$

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[1] Howard, Hodgkin J. Chem. Soc., **41**, 66, Ber. d. chem. Ges., **15**, Ref. 379

[2] Hesse Ann. Chem. (Liebig), **225**, 104

[3] Howard, Hodgkin J. Chem. Soc., **41**, 66, Ber. d. chem. Ges., **15**, Ref. 734

[4] Cazeneuve: Bull. soc. chim., **49**, 97

[5] Hesse Ann. Chem. (Liebig), **205**, 317

[6] Hesse *Loc. cit.*, p. 358.

[7] Hesse *Loc. cit.*, p. 323.

[8] Lippmann Ber. d. chem. Ges., **28**, 1972

[9] Hesse, p. 337.

[10] Hesse, p. 341.

CHITENINE, $C_{19}H_{22}N_2O_4 + 4H_2O$. Crystals

Alcohol ($d = 0.958$) .... $p = 0.1093$, $d = 0.9595$, $[\alpha]_D = -142.7°$ [1]

QUINICINE, $C_{20}H_{24}N_2O_2$. Amorphous; melting-point, 60°.

Chloroform .... $c = 2$, $[\alpha]_D^{15} = +44.1°$ [2]

Oxalate, $(C_{20}H_{24}N_2O_2)_2C_2H_2O_4 + 9H_2O$. Crystals

Chloroform-alcohol mixture ... $c = 1$ to 3, $[\alpha]_D^{15} = +20.68 - 1.14c$ [3]
Water .... $c = 2$, " $= +9.54$
Water + 2 mol. H_2SO_4 .... $c = 2$, " $= +15.54$

QUINIDINE (Conquinine). $C_{20}H_{24}N_2O_2$. Crystals (from benzene); melting-point, 171.5° (corr.).

1 vol. alcohol (97 vol. p. c.) + 2 vol. chloroform { $p = 2.1$, $[\alpha]_D^{16.9} = +269.7°$; $p = 1.06$, $[\alpha]_D^{17} = +274.7$ [4]
Benzene .... $c = 1.62$, " $= +195.2$ [5]
Toluene .... $c = 1.62$, " $= +206.6$
Chloroform .... $c = 1.62$, " $= +228.8$

Alcohol (wt. p. c.)	100.0	95.3	90.5	85.0	80.0	75.0
$[\alpha]_D^{17} =$	$+255.4°$	257.6	259.0	259.4	259.3	259.4 [6]

Alcohol (97 vol. p. c.) .... $c = 1$ to 3, $[\alpha]_D^{15} = +269.57 - 3.60c$ [7]
Chloroform .... $c = 1.756$, " $= +230.35°$

Alcohol, $[\alpha]_j = 268.6°$; methyl alcohol, $[\alpha]_j = 257.5°$. Wyrouboff[8] explains this difference by formation of alcoholates: $(C_{20}H_{24}N_2O_2)CH_4O$, $[\alpha]_j = +236.1°$ and $(C_{20}H_{24}N_2O_2)C_2H_6O$, $[\alpha]_j = +235.3°$.

$C_{20}H_{24}N_2O_2 + 2^1/_2H_2O$ (from water):

Alcohol (97 vol. p. c.) .... $c = 1$ to 3, $[\alpha]_D^{15} = +236.77 - 3.01c$ [9]
" (80 " .... $c = 2$, " $= +232.7°$
Chloroform-alcohol mixture .. $c = 1$, " $= +244.5$
" " " ..... $c = 2$, " $= +241.75$

Neutral Hydrochloride, $C_{20}H_{24}N_2O_2.HCl + H_2O$. Asbestos-like prisms

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[1] Skraup Ann. Chem. (Liebig), **199**, 352
[2] Hesse Ibid., **178**, 260.
[3] Hesse, p. 261
[4] Lenz Ztschr. anal. Chem., **27**, 571
[5] Oudemans. Ann. Chem. (Liebig), **182**, 44
[6] Oudemans, *Ibid.*, **182**, 48
[7] Hesse *Ibid.*, **176**, 203, **182**, 128
[8] Compt. rend., **115**, 832
[9] Hesse *Loc. cit.*

Water	$c = 1$ to 2,	$[\alpha]_D^{15} = +205.83 - 4.93c$	[1]
Calculated for alkaloid,		" $= +240.45 - 6.60c$	
Water + 2 mol. HCl for 1 mol. alkaloid	$c = 1$ to 5,	" $= +292.56 - 3.09c$	
Calculated for alkaloid		" $= +338.37 - 4.52c$	
Alcohol (97 vol p. c.)	$c = 2$ to 5,	" $= +212.0 - 2.56c$	
" (80 ")	$c = 2$	" $= +230.25$	

$C_{20}H_{24}N_2O_2.HCl + 2H_2O$. $c = 2.0$ (anhydrous)·

		Water,	Abs alcohol	Alcohol (90.5 wt p. c.).	
Salt ($c = 1.58$ alkaloid),	$[\alpha]_D^{17} =$	$+190.8°$	199.4°	213.0°	[2]
Alkaloid (calc.)	" $=$	$+233.6$	244.1	260.7	

Acid Hydrochloride, $C_{20}H_{24}N_2O_2.2HCl + H_2O$. Prisms.

Water . . . . . $c = 2$, $[\alpha]_D^{15} = +250.3°$ [3]

Neutral Sulphate, $(C_{20}H_{24}N_2O_2)_2.H_2SO_4 + 2H_2O$. Prisms.

Water	$c = 1$	$[\alpha]_D^{15} = +179.54°$	[4]
	alkaloid,	" $= +215.55$	
4 mol. HCl + water,	$c = 2$ (anhydrous),	" $= +286.4$	
	alkaloid,	" $= +329.8$	
5 mol. H_2SO_4 + water,	$c = 2$ (anhydrous),	" $= +281$	
	alkaloid,	" $= +323$	
Absolute alcohol	$c = 2.8$ (anhydrous),	$[\alpha]_D^{17} = +211.5$	[5]
	alkaloid,	" $= +255.2$	
Alcohol (80 vol. p. c.)	$c = 2$,	$[\alpha]_D^{15} = +218.2°$	[6]
" (60 ")	$c = 2$,	" $= +227.0$	
Chlorof.-alcohol mix.	$c = 2$,	" $= +209.25$	
Chloroform	$c = 3$ (anhydrous),	" $= +184.2$	
"	$c = 5$,	" $= +180.1$	

Acid Sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4 + 4H_2O$. Asbestos-like needles.

Water	$c = 2$ to 8,	$[\alpha]_D^{15} = +212.0 - 0.8c$	[6]
	alkaloid,	" $= +323.23 - 1.86c$	
2 mol. H_2SO_4 + water	$c = 1$ to 10,	" $= +215.49 - 1.41c$	
	alkaloid,	" $= +328.55 - 3.27c$	
Alcohol (97 vol. p. c.)	$c = 2$,	" $= +183°$	

Nitrate, $C_{20}H_{24}N_2O_2.HNO_3$. Short thick prisms

Absol. alcohol, $c = 2.17$, $[\alpha]_D^{17} = +199.3$, alkaloid, $[\alpha]_D^{17} = +232.6°$ [6]

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[1] Hesse Ann. Chem (Liebig), 176, 225

[2] Oudemans *Ibid*, 182, 49.

[3] Hesse · *Loc cit*

[4] Hesse.

[5] Oudemans

[6] Oudemans *Loc cit.*

Oxalate, $(C_{20}H_{24}N_2O_2)_2C_2H_2O_4 + H_2O$. Very small crystals.
Chloroform-alcohol mixture… $c = 1$ to 3, $[\alpha]_D^{15} = + 189.0 - 2.18\,c$[1]

Acetyl Quinidine, $C_{20}H_{23}(C_2H_3O)N_2O_2$. Amorphous.
Alcohol (97 vol. p. c.)…. $c = 2$, $[\alpha]_D^{15} = + 127.6°$[2]
3 mol. HCl + water…… $c = 2$, " $= + 158.6$

APOQUINIDINE, $C_{19}H_{22}N_2O_2 + 2H_2O$. Amorphous; melting-point, 137°.
Alcohol (97 vol. p. c.)…… $c = 2$ (anhydrous), $[\alpha]_D^{15} = + 155.3°$[3]
3 mol. HCl + water……… $c = 2$ " " $= + 216.5$

Diacetylapoquinidine, $C_{19}H_{20}(C_2H_3O)_2N_2O_2$. Resin; melting-point, 60°.
Alcohol (97 vol. p. c.)…… $c = 2$, $[\alpha]_D^{15} = + 40.4°$[4]
3 mol. HCl + water…….. $c = 2$, " $= + 78.4$

Hydrochlorapoquinidine, $C_{19}H_{23}ClN_2O_2 + 2H_2O$. Crystals, melting-point, 164°
Alcohol (97 vol. p. c.) …….. $c = 2$ (anhydrous), $[\alpha]_D^{15} = + 203.7°$[5]
3 mol. HCl + water …….. $c = 2$ " " $= + 258.4$

Diacetylhydrochlorapoquinidine, $C_{19}H_{21}(C_2H_3O)_2ClN_2O_2$ Rhombic leaves (from ether); melting-point, 168°.
3 mol. HCl + water ………… $c = 2$, $[\alpha]_D^{15} = + 94.6°$[6]

CINCHONINE, $C_{19}H_{22}N_2O$. Crystals; melting-point, 255.4° (corr.)[7]
Alcohol (97 vol. p. c.) ……… $c = 0.5$, $[\alpha]_D^{15} = + 226.26°$[8]
$c = 1$, " $= + 225.96$
Chloroform-alcohol mixture…. $c = 1$ to 5, " $= + 238.8 - 1.46\,c$
Absolute alcohol …… $c = 0.5$ to 0.75, $[\alpha]_D^{17} = + 223.3°$[9]
Chloroform ………… $c = 0.455$, " $= + 214.8$
" ………… $c = 0.535$, " $= + 212.3$
" ………… $c = 0.560$, " $= + 209.6$
Chlorof.-alcohol mixture $p = 1.061$, $d_4^{19.8} = 1.2508$, $[\alpha]_D^{19.8} = + 239.40°$[10]
" " " $p = 2.123$, $d_4^{20.2} = 1.2497$, $[\alpha]_D^{20.2} = + 234.55$
Absolute alcohol …… $c = 0.4715$, $[\alpha]_D^{?} = + 222.92°$[11]

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[1] Hesse
[2] Hesse Ann. Chem. (Liebig), **205**, 318
[3] Hesse *Ibid.*, p. 326
[4] Hesse *Ibid.*, p. 327
[5] Hesse *Ibid.*, p. 343
[6] Hesse *Ibid.*, p. 352
[7] Lenz, Ztschr. anal. Chem., **27**, 572
[8] Hesse Ann. Chem. (Liebig), **176**, 228
[9] Oudemans *Ibid.*,, **182**, 44
[10] Lenz *Loc. cit.*
[11] Pum Wien. Monatsh. Chem., **13**, 683

From benzoyl cinchonine.

Absolute alcohol............ $c = 0.75$, $[\alpha]_D^{17} = +233.1^\circ$[1]

Neutral Hydrochloride, $C_{19}H_{22}N_2O.HCl + 2H_2O$. Rhombic crystals.

Water ... . $c = 0.5$ to 3, $[\alpha]_D^{15} = +165.50 - 2.425\,c$[2]
alkaloid, " $= +204.46 - 3.7\,c$
2 mol. HCl + water ...... $c = 1$ to 7, " $= +214.0 - 1.72\,c$
alkaloid, " $= +264.37 - 2.625\,c$
Alcohol (97 vol. p. c.) $c = 1$ to 10, $[\alpha]_D^{15} = 179.81 - 6.314c + 0.8406c^2 - 0.0371\,c^3$
" (80 ") $c = 2$, " $= +188.9^\circ$
" (60 ") $c = 2$, " $= +195.5^\circ$
Chlorof.-alcohol mixt $c = 2$, " $= +152.0$

Acid Hydrochloride, $C_{19}H_{22}N_2O\ 2HCl$ Prisms.

Water .... $c = 3$, $[\alpha]_D^{15} = +206.1^\circ$[3]

Neutral Sulphate, $(C_{19}H_{22}N_2O)_2.H_2SO_4 + 2H_2O$ Monoclinic crystals.

Water .... $c = 1$ to 2, $[\alpha]_D^{15} = +170.3 - 0.855\,c$[4]
alkaloid, " $= +206.79 - 1.26\,c$
$2^1/_2$ mol H_2SO_4 + water.. $c = 0.5$ to 6, " $= +219.10 - 1.85\,c$
alkaloid, " $= +266.07 - 2.69\,c$
Alcohol (97 vol p c)..... $c = 3$ to 10, " $= +193.29 - 0.374\,c$
" (80 ")..... $c = 2$, " $= +202.95$
" (60 ") ... $c = 2$, " $= +204.14$
Chloroform-alcohol mixture. $c = 2$, " $= +185.25$

According to Wyrouboff,[5] the sulphate and selenate of cinchonine ($[\alpha]_j = 234^\circ$) take up one molecule of crystallization alcohol from alcoholic solution.

$$(C_{19}H_{22}N_2O)_2H_2SO_4 + C_2H_6O,\quad [\alpha]_j = +185^\circ;$$
$$(C_{19}H_{22}N_2O)_2H_2SeO_4 + C_2H_6O,\quad \text{"} = +182.5^\circ.$$

Oxalate, $(C_{10}H_{22}N_2O)_2C_2H_2O_4 + 2H_2O$. Prisms.

Chloroform-alcohol mixture. ... $c = 1$ to 3, $[\alpha]_D^{15} = 165.46 - 0.763\,c$[6]

Wyrouboff[7] gives, also, the constants of rotation of cinchonine salts which have separated from different solutions combined in crystalline form with part of the solvent

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[1] Léger Compt rend., **117**, 110
[2] Hesse Ann Chem (Liebig), **176**, 230
[3] Hesse *Ibid.*, **276**, 91
[4] Hesse. *Ibid*, **176**, 231
[5] Compt rend, **115**, 832
[6] Hesse Ann. Chem. (Liebig), **176**, 232
[7] Ann. chim phys., [7], **1**, 5

Diisobutylcinchoninehydrobromide, $C_{19}H_{22}N_2O\ C_4H_9Br + H_2O$ Melting-point, 176°

Water . . . . $p = 1$, $[\alpha]_D^{17} = +125°$ [1]

Acetylcinchonine, $C_{19}H_{21}(C_2H_3O)N_2O$. Amorphous

Alcohol (97 vol. p. c.) . . . $c = 2$, $[\alpha]_D^{15} = +114.1°$ [2]
3 mol. HCl + water . . . . . $c = 2$, " $= +139.5$

Hydrochlorcinchoninedihydrochloride, $C_{19}H_{23}ClN_2O \cdot 2HCl$. Monoclinic crystals

Water . . . . $c = 3$, $[\alpha]_D^{15} = +185.9°$ [3]
1 mol. HCl + water . . . . $c = 2.4$, " $= +187$

β-CINCHONINE. $C_{19}H_{22}N_2O$. Probably identical with one of the bases made by Jungfleisch and Léger (see below). Crystals; melting-point, 250° to 252°.

Absolute alcohol . . . . $c = 0.4715$, $[\alpha]_D = +195.77°$ [4]

δ-CINCHONINE, $C_{19}H_{22}N_2O$ Prisms; melting-point, 150°.

Alcohol (97 p. c.) . . . . . . $c = 1$, $[\alpha]_D^{17} = +125.2°$ [5]
2 mol. HCl + water . . $c = 1$, " $= +176.9$
4 " " + " . . $c = 1$, " $= +178.2$

α-ISOCINCHONINE (Cinchoniline), $C_{19}H_{22}N_2O$. Anhydrous monoclinic crystals; melting-point, 126°;[6] 125° to 127°;[7] 130.4° (corr.).[8]

Absolute alcohol . . . . $c = 3$, $[\alpha]_D^{15} = +51.6°$ [9]
Alcohol (97 p. c.) . . . . $c = 1$, " $= +53.22$ [10]
" " . . . . . . $c = 0.5$, $[\alpha]_D^{16} = +50.3$

According to Hesse, this last value is wrong, because, as he finds, the rotation increases with increasing dilution.

2 mol. HCl + water . . . . . . $c = 1$, $[\alpha]_D^{16} = +59.15°$ [10]
4 " " + " . . . . . . $c = 1$, " $= +63.10$

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[1] Vial. J. pharm. Chim., [5], **30**, 52.
[2] Hesse. Ann. Chem. (Liebig), **205**, 321
[3] Hesse. *Ibid.*, **276**, 110
[4] Pum. Wien. Monatsh. Chem., **13**, 683
[5] Jungfleisch, Léger. Compt. rend., **118**, 31
[6] Hesse. Ann. Chem. (Liebig), **276**, 93
[7] Comstock, Königs. Ber. d. chem. Ges., **20**, 2521
[8] Jungfleisch, Léger. Compt. rend., **106**, 658
[9] Hesse
[10] Jungfleisch, Léger

Hydrochloride, $C_{19}H_{22}N_2O.HCl + 2$ or $3H_2O$. Prisms; melting-point, 226°.

In pure aqueous solution, the salt with 2 molecules of water, for $c = 2.5$, and the salt with 3 molecules, for $c = 4$, do not rotate the plane of polarized light.

Salt with 2 mol. H_2O.

3 mol HCl + water, $c = 4$, $[\alpha]_D^{15} = +40.6°$; alkaloid, $[\alpha]_D^{15} = +50.6°$[1]

Salt with 3 mol. H_2O.

Water	$c = 1$,	$[\alpha]_D^{16}$	$+5.0°$	[2]
2 mol. HCl + water	$c = 1$,	"	$+59.3$	
4 " " + "	$c = 1$,	"	$= +63.1$	

From this difference in optical behavior, Hesse concludes that α-isocinchonine is different from cinchoniline.

Chlor-α-isocinchonine, $C_{19}H_{21}ClN_2O$. Anhydrous colorless prisms; melting-point, 172°.

Absolute alcohol............ $c = 1.868$, $[\alpha]_D^{15} = +67.6°$[3]

β-ISOCINCHONINE (Cinchonigine), $C_{19}H_{22}N_2O$. Prisms; melting-point, 125°.

Absolute alcohol....	$c = 1$,	$[\alpha]_D^{15}$	$53.12°$	[1]
" "	$c = 3$,	"	$= -55.10$	

Colorless prisms; melting-point, 128° (corr.).

Alcohol (97 p. c.)..........	$c = 1$,	$[\alpha]_D^{17}$	$= -60.1°$	[5]
" "	$c = 0.5$,	$[\alpha]_D^{15}$	-61.16	
2 mol. HCl + water.....	$c = 1$,	"	$= -40$	
4 " " + "	$c = 1$,	"	$= -38.21$	

Hydrochloride, $C_{19}H_{22}N_2O.HCl + H_2O$. Prisms; melting-point, 201°.

Water................	$c = 1$,	$[\alpha]_D^{15}$	$= -68.10°$	[6]
"	$c = 2$	"	$= -71.03$	
2 mol. HCl + water...	$c = 2$	"	$= -28.3$	
2 " " + " ...	$c = 5$	"	$= -34.0$	
5 " " + " ...	$c = 2$	"	$= -27.9$	
Chloroform...........	$c = 2$	"	$= -149$	

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[1] Hesse.

[2] Jungfleisch, Léger.

[3] Hesse: Ann. Chem. (Liebig), 276, 97.

[4] Hesse: *Ibid.*, 260, 215

[5] Jungfleisch, Léger. Compt. rend., 106, 358.

[6] Hesse: Ann. Chem. (Liebig), 260, 216.

As distinguished from all other di-acid cinchona alkaloids the rotating power of this alkaloid increases with the concentration, but decreases with increase of acid.

$C_{19}H_{22}N_2O.HCl + 2H_2O$. Colorless, prismatic needles; melting-point, 213° (corr.).

Water .... $c = 1$, $[\alpha]_D^{15} = -65.41°$ [1]

CINCHONIDINE, $C_{19}H_{22}N_2O$. Needles.

Alcohol (97 p. c.) .... $c = 0.75$, $[\alpha]_D = +195.0°$ [2]
Alcohol .... $c = 0.75$, $[\alpha]_D^{17} = +201.4°$ [3]
2 HCl + water .... $p = 1$, " $= +228.9$
2 HCl + " ..... $p = 1.5$ " $= +225.13$
4 HCl + " ..... $p = 1$, " $= +226.3$

APOCINCHONINE, $C_{19}H_{22}N_2O$. Prisms, melting-point, 209°;[4] 228°[5].

Alcohol (97 p. c.) .... $c = 1$, $[\alpha]_D^{15} = +160.0°$ [6]
2 mol. HCl + water .... $c = 2$, " $= +212.5$
3 " " + " ..... $c = 2$, " $= +212.3$
Chloroform mixture .... $c = 3$, " $= +197.5$ [7]
Absolute alcohol ...... $c = 1.56$, $[\alpha]_D^{15} = +159.7$ [8]

Hydrochloride, $C_{19}H_{22}N_2O.HCl + 2H_2O$. Needles.

Water ... $c = 0.006$, $[\alpha]_D^{16} = -139.0°$, alkaloid, $[\alpha]_D^{16} = +171.9°$
.... $c = 0.01$, " $= -138.5$, " " $= +171.3$
.... $c = 0.015$ " $= -138.5$; " " $= +171.3$

Hydrobromide, $C_{19}H_{22}N_2O.HBr + H_2O$. Needles.

Water ...... $c = 0.0076$, $[\alpha]_D^{16} = -126.2°$, alkaloid, $[\alpha]_D^{16} = +168.7°$

Hydroiodide, $C_{19}H_{22}N_2O.HI + H_2O$. Needles.

Water ...... $c = 0.006$, $[\alpha]_D^{16} = -117.2°$, alkaloid, $[\alpha]_D^{16} = +175.5°$

Sulphate, $(C_{19}H_{22}N_2O)_2.H_2SO_4 + 3H_2O$. Needles.

Water ...... $c = 0.0045$, $[\alpha]_D^{16} = -130.0°$, alkaloid, $[\alpha]_D^{16} = +164.0°$

Chlorate, $C_{19}H_{22}N_2O.HClO$. Needles.

Water ...... $c = 0.0069$, $[\alpha]_D^{16} = -129.0°$; alkaloid, $[\alpha]_D^{16} = +166.2°$

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[1] Jungfleisch, Léger, Compt. rend., **106**, 357.
[2] Jungfleisch, Léger, Ibid., **105**, 1255; Bull. soc. chim., **49**, 747.
[3] Jungfleisch, Léger, Compt. rend., **118**, 536.
[4] Hesse, Ann. Chem. (Liebig), **205**, 3[illegible].
[5] Hesse, Ibid., **276**, 115.
[6] Hesse, Ibid., **205**.
[7] Hesse, Ibid., **276**.
[8] Oudemans, Rec. trav. chim. Pays-Bas, **1**, 175.

Perchlorate, $C_{19}H_{22}N_2O.HClO_4 + H_2O$. Needles.
Water....... $c = 0.0052$, $[\alpha]_D^{16} = +124.9°$; alkaloid, $[\alpha]_D^{16} = +175.3°$ [1]

Oudemans[1] studied, further, the effect of acids (HCl, HBr, HNO_3, $HClO_3$, $HClO_4$, CH_2O_2, $C_2H_4O_2$, H_2SO_4, $C_2H_2O_4$, H_3PO_4, $C_6H_8O_7$) on the rotation of apocinchonine.

Acetylapocinchonine, $C_{19}H_{21}(C_2H_3O)N_2O$ Crystals

Alcohol (97 vol. p. c.)...... $c = 2$, $[\alpha]_D^{15} = +71.4°$ [2]
3 mol. HCl + water .... $c = 2$, " $= +97.9$

Chlorapocinchonine, $C_{19}H_{23}ClN_2O$ Needles, melting-point, 197°

Alcohol (97 vol. p. c.) ... $c = 0.5$, $[\alpha]_D^{15} = +205.4°$ [3]
3 mol. HCl + water...... $c = 2$, " $= +208.0$
Alcohol (97 vol. p. c.).... $c = 0.4745$, $[\alpha]_D^{18} = +211°$ [1]
" " ... $c = 0.2655$, $[\alpha]_D^{16} = +210$

Neutral Hydrochloride, $C_{19}H_{23}ClN_2O.HCl + H_2O$ Needles.
Water..... . $c = 0.0045$, $[\alpha]_D^{16} = +165.9°$; alkaloid, $[\alpha]_D^{16} = +193.2°$

Acid Hydrochloride, $C_{19}H_{23}ClN_2O.2HCl$ Prisms.
Water...... $c = 0.0197$, $[\alpha]_D^{16} = +185.0°$, alkaloid, $[\alpha]_D^{16} = +226°$

Sulphate, $(C_{19}H_{23}ClN_2O)_2H_2SO_4 + 3H_2O$. Needles
Water.... $c = 0.005$, $[\alpha]_D^{16} = +156.6°$, alkaloid, $[\alpha]_D^{16} = +192.5°$

Nitrate, $C_{19}H_{23}ClN_2O.HNO_3$. Needles
Water.... $c = 0.005$, $[\alpha]_D^{16} = +173.5°$, alkaloid, $[\alpha]_D^{16} = +194.8°$

Chlorate, $C_{19}H_{23}ClN_2O.HClO_3$ Crystals
Water....... $c = 0.005$, $[\alpha]_D^{16} = +155.3°$, alkaloid, $[\alpha]_D^{16} = +194.9°$ [4]

On the effect of acids (HCl, HBr, HNO_3, $HClO_3$, $HClO_4$, CH_2O_2, $C_2H_4O_2$, H_2SO_4, $C_2H_2O_4$, H_3PO_4, $C_6H_8O_7$) on the specific rotation of chlorapocinchonine, see paper of Oudemans.[4]

Acetyl Chlorapocinchonine, $C_{19}H_{22}(C_2H_3O)ClN_2O$ Amorphous varnish.

Alcohol (97 vol. p. c.).... $c = 2$, $[\alpha]_D^{15} = +108.0°$ [5]
3 mol. HCl + water ... $c = 2$, " $= +118.8$

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[1] Oudemans *Loc. cit.*
[2] Hesse Ann. Chem. (Liebig), **205**, 338.
[3] Hesse *Ibid.*, p. 349
[4] Oudemans Rec. trav. chim. Pays-Bas, **1**, 182
[5] Hesse Ann. Chem. (Liebig), **205**, 354.

DIAPOCINCHONINE, $C_{38}H_{44}N_4O_2$. Amorphous.

Alcohol (97 vol. p. c.) .... $c = 2$, $[\alpha]^{15}_{D} = + 20.0°$ } [1]
3 mol HCl + water .... $c = 2$, " $= + 23.6$ }

Jungfleisch and Léger[2] look upon this body as a mixture of several bases, Hesse,[3] however, not.

Diacetylapocinchonine, $C_{38}H_{42}(C_2H_3O)_2N_4O_2$. Yellow varnish like mass.

Inactive in 2 per cent. alcoholic solution.

3 mol HCl + water .... $c = 2$, $[\alpha]^{15}_{D} = + 26.1°$ [4]

ISOAPOCINCHONINE, $C_{19}H_{22}N_2O$. Anhydrous prisms, melting-point, 223° to 224°.

Absolute alcohol .... $c = 3$, $[\alpha]^{15}_{D} = + 186.2°$ [5]

APOISOCINCHONINE, $C_{19}H_{22}N_2O$. Anhydrous white needles; melting-point, 216°.

Absolute alcohol .... $c = 3$, $[\alpha]^{15}_{D} = + 166.8°$ [6]

Chlorapoisocinchonine, $C_{19}H_{21}ClN_2O$. Anhydrous white needles; melting-point, 203°

Absolute alcohol ...... $c = 3$, $[\alpha]^{15}_{D} = + 189.8°$

Dihydrochloride, $C_{19}H_{21}ClN_2O.2HCl$ Anhydrous crystals.

Water .... $c = 3$, $[\alpha]^{15}_{D} = + 172.5°$ [7]

HOMOCINCHONINE, $C_{19}H_{22}N_2O$. Prisms; melting-point, 251°.

2 vol chloroform + 1 vol absolute alcohol .. $c = 3$, $[\alpha]^{15}_{D} = + 208.9°$

Hydrochloride, $C_{19}H_{22}N_2O.HCl + 2H_2O$. Needles.

Alcohol (97 vol p. c.) . ... $c = 3$, $[\alpha]^{15}_{D} = + 159.7°$

Dihydrochloride, $C_{19}H_{22}N_2O.2HCl$. Prisms.

Water .... $c = 2.528$, $[\alpha]^{15}_{D} = + 198.5°$ [8]

PSEUDOCINCHONINE, $C_{19}H_{22}N_2O$. Anhydrous white needles; melting-point, 232°

2 vol chloroform + 1 vol. absolute alcohol ... $c = 3$, $[\alpha]^{15}_{D} = + 198.4°$

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[1] Hesse Ann Chem (Liebig), 205, 333
[2] Compt rend 114, 1192
[3] Ann Chem (Liebig), 276, 1[illegible]
[4] Hesse *Ibid* 205, 334
[5] Hesse *Ibid*, 276, 1[illegible]7
[6] Hesse *Ibid* 276, 100
[7] Hesse *Ibid*, 276, 102
[8] Hesse *Ibid* 276, 104 and 105

Dihydrochloride, $C_{19}H_{22}N_2O\,2HCl$. Prisms.

Water .... $c = 3$, $[\alpha]_D^{15} = +189.3°$ [1]

α-OXYCINCHONINE, $C_{19}H_{22}N_2O_2$. Colorless flattened prisms.

Alcohol (97 vol p c) .. .. $c = 1$, $[\alpha]_D^{18} = +182.56°$
2 mol HCl + water............. $c = 1$, $[\alpha]_D^{19} = +210.76$

Hydrochloride, $C_{19}H_{22}N_2O_2.HCl$. Colorless needles, melting-point, 230°, with decomposition.

1 mol. HCl + water .... $c = 1$, $[\alpha]_D^{13} = +174.37°$ [2]

β-OXYCINCHONINE, $C_{19}H_{22}N_2O_2$. Needles; melting-point, 273°.

Alcohol (97 vol p c.).. ..... $c = 1$, $[\alpha]_D^{'} = +187.14°$ [3]
$[\alpha]_D = +188.8°$ [4]

CINCHOTENINE, $C_{18}H_{20}N_2O_3 + 3H_2O$(?). Crystals; melting-point, 197° to 198°.

Chloroform-alcohol mixture.. $c = 2$, $[\alpha]_D^{15} = +115.5°$ [5]
2 mol H_2SO_4 + water ...... $c = 2$, " $= +175.5$

CINCHOTENICINE, $C_{18}H_{20}N_2O_3$. Dark brown amorphous mass; melting-point, 153° (uncorr.).

Water ... . $c = 2.614$, $[\alpha]_D^{15} = +0.9°$ [6]

CINCHOTENIDINE, $C_{18}H_{20}N_2O_3 + 3H_2O$. Monoclinic prisms; melting-point, 256° (corr.).

Water.... .... $p = 0.212$ $[\alpha]_D^{''} = -189°$ [7]
3 mol HCl + water. . $c = 5$ (anhydrous), $[\alpha]_D^{15} = -201.4°$ [8]

CINCHONICINE, $C_{19}H_{22}N_2O$ Tough yellowish mass.

Alcohol (95 vol. p c.). ... $c = 1$, $[\alpha]_D^{15} = +48°$ [9]
Chloroform............... $c = 2$, " $= +46.5$

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[1] Hesse Ann Chem (Liebig), **276**, 107 and 108
[2] Jungfleisch, Léger Compt rend, **108**, 952
[3] Jungfleisch, Léger Compt rend, **105**, 1257, Bull soc chim, **49**, 747.
[4] Jungfleisch, Léger Compt rend, **119**, 1264.
[5] Hesse Ann Chem (Liebig), **176**, 233
[6] Hesse Ber d. chem Ges, **11**, 1983
[7] Skraup, Vortmann Ann Chem (Liebig), **197**, 240
[8] Hesse Ber d. chem Ges, **14**, 1893 (note)
[9] Hesse Ann Chem (Liebig), **178**, 262.

Roques obtained it in crystalline condition, and found .

Alcohol.................. $[\alpha]_D = + 48\ 25°$ [1]
2 mol HCl + water.... " $= + 28\ 72$

Oxalate, $(C_{19}H_{22}N_2O)_2C_2H_2O_4 + 3(?)H_2O$. Crystals.

Alcohol (97 vol p c)... .. $c = 2$, $[\alpha]^{15}_D = + 23\ 5°$ [2]
Chloroform-alcohol mixture $c = 1$ to 3, " $= + 23\ 1$
Water .... $c = 2$, " $= + 22\ 6$
2 mol. H_2SO_4 — water . .. $c = 2$, " $= + 25\ 75$

CINCHONIDINE, $C_{19}H_{22}N_2O$. Crystals, melting-point, 207. (corr.),[3] 200° to 201°,[4] 210.5°.[5]

Alcohol (97 vol p. c)....... $c = 1$ to 5, $[\alpha]^{15}_D = - 107.48 + 0\ 297\ c$
" (95 " ")....... $c = 2$, " $= - 113\ 53 + 0\ 426\ c$
" (80 " ")....... $c = 2$, " $= - 119.5$
Chloroform-alcohol mixture $c = 2$, " $= - 108.9$
Chloroform .... $c = 2$, " $= - 83.9$

Absolute alcohol c =	1 5	2	2 5	3	3 5	4
t = 15°	— 110.0°	109.6°	109.2°	108 8°	108.4°	108 0°
20	— 109 0	108.6	108.2	107.8	107.4	107 0
Alcohol (wt. p c)		100.0	90.5	80 2	70 8	60 0
For c = 1 54, $[\alpha]^{17}_D$ =		— 109.6°	115 0	117 8	120.4	121 1

Chloroform...... $c = 1\ 545$, $[\alpha]^{17}_D = - 77.3°$
" ...... $c = 3\ 41$, " $= - 74\ 0$
Chloroform-alcohol mixture... $p = 1\ 1$ to 2 1, $[\alpha]^{17\ 2-18\ 4°}_D = - 107\ 9$
Chloroform .... $c = 4$, $[\alpha]^{15}_D = - 70\ 0°$ [9]
3 mol HCl — water....... . $c = 5$, " $= - 174\ 6$

Hydrochloride, $C_{19}H_{22}N_2O.HCl + H_2O$. Triclinic crysta

Water .... $c = 1$ to 3, $[\alpha]^{15}_D = - 105\ 34 + 0.76\ c$
alkaloid, " $= - 123\ 98 + 1\ 05\ c$
Water — 2 mol HCl... $c = 1$ to 10, " $= - 154\ 07 + 1\ 39\ c$
alkaloid, " $= - 181\ 32 + 1\ 925\ c$
Alcohol (97 vol p. c) .... $c = 3$, $[\alpha]^{15}_D = - 108.0°$
" (80 " ") .... $c = 2$, " $= - 135.25$
Chloroform .... $c = 2.85$ (anhydrous), " $= - 24\ 2$
2 mol HCl — water...... $c = 10$, $[\alpha]^{20}_D = - 142\ 1°$

[1] Compt rend, **120**, 1170
[2] Hesse Ann Chem (Liebig), **178**, 263.
[3] Lenz Ztschr anal Chem **27**, 565
[4] Hesse Ber d chem Ges, **14**, 1891
[5] Skraup Vortmann Ann Chem (Liebig), **197**, 229
[6] Hesse *Ibid*, **176**, 219.
[7] Oudemans *Ibid*, **182**, 44.
[8] Lenz *Loc. cit*
[9] Hesse Ann Chem (Liebig), **205**, 196
[10] Hesse *Ibid*, **176**, 220

Salt, $C_{19}H_{22}N_2O.HCl + 2H_2O$.

Water.......... ..... $c = 1.54$ to 1.62 (calculated as alkaloid),[1]
$[\alpha]_D^{17} = -104.6°$ (anhydrous); alkaloid, $[\alpha]_D^{17} = -129.2°$

Absolute alcohol....... $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -99.9°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -123.5°$

Alcohol (89 wt p. c.). $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -119.6°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -147.7°$

Alcohol (80 wt p. c).. $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -128.7°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -159.0°$

Neutral Sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4 + 6H_2O$. Glistening prisms.

Water .... $c = 1.06$, $[\alpha]_D^{15} = -106.77$, alkaloid, $[\alpha]_D^{15} = -142.31°$

Salt with 3 Mol. Water.

Alcohol (80 vol p c)........ $c = 2$, $[\alpha]_D^{15} = -144.5°$ [2]

Absolute alcohol....... $c = 1.54$ to 1.62 (calculated as alkaloid),[1]
$[\alpha]_D^{17} = -118.7°$ (anhydrous); alkaloid, $[\alpha]_D^{17} = -157.5°$

Alcohol (89 wt. p c).. $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -128.7°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -171.8°$

Alcohol (80 wt p c).. $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -131.2°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -175.1°$

Acid Sulphate, $C_{19}H_{22}N_2O\ H_2SO_4 + 5H_2O$ Large prisms

Water. . .. . $c = 2$, $[\alpha]_D^{15} = -110.5°$,[3]
alkaloid, $[\alpha]_D^{15} = -177.95°$

Alcohol (80 vol p c). .. $c = 2$, $[\alpha]_D^{15} = -109.0°$

Chloroform-alcohol mixture $c = 2$, " $= -101.0$

Disulphate, $C_{19}H_{22}N_2O\ 2H_2SO_4 + 2H_2O$ Small prisms

Water, $c = 1$ to 7, $[\alpha]_D^{15} = -105.96 + 1.0267c - 0.03376c^2 + 0.00104c^3$ [4]
Alkaloid, " $= -185.77 + 3.1557c - 0.18158c^2 + 0.00981c^3$

Nitrate, $C_{19}H_{22}N_2O\ HNO_3 + H_2O$ Large prisms

Water ... . $c = 1.54$ to 1.62 (calculated as alkaloid),[1]
$[\alpha]_D^{17} = -99.9°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -126.3°$

Absolute alcohol....... $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -103.2°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -130.4°$

Alcohol (89 wt p c)... $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -119.0°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -150.4°$

Alcohol (80 wt p c.).. $c = 1.54$ to 1.62 (calculated as alkaloid),
$[\alpha]_D^{17} = -127.0°$ (anhydrous), alkaloid, $[\alpha]_D^{17} = -160.4°$

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[1] Oudemans Ann Chem. (Liebig), 182, 46

[2] Hesse *Ibid*, 176, 221

[3] Hesse *Ibid*, 176, 222

[4] Hesse *Loc cit*

Oxalate, $(C_{19}H_{22}N_2O)_2C_2H_2O_4 + 2H_2O$. Prisms

Chloroform-alcohol mixture, $c = 1$ to 3, $[\alpha]_D^{15} = -98.7°$ [1]

Oudemans[2] has made observations on the changes wh take place in the specific rotation of quinine, quinidine, c chonine and cinchonidine in presence of variable amounts HCl, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4, H_3PO_4, $HCHO_2$, a $H_2C_2O_4$ Also similar observations on quinamine and c quinamine.[3]

Wyrouboff[4] has published numerous observations on cinch idine salts, which, on crystallizing from different solvents, co bine with varying amounts of the latter.

Acetylcinchonidine, $C_{19}H_{21}(C_2H_3O)N_2O$. Brittle mass; me ing-point, 42°.

Alcohol (97 vol p c.)………… $c = 2$, $[\alpha]_D^{15} = -38.4°$ [5]
1 mol. HCl + water ……… …. $c = 2$, " $= -66.6$
3 " " + " …. ……. $c = 2$, " $= -81.3$

Cinchonidine Sulphonic Acid, $C_{19}H_{21}N_2O.HSO_3 + H_2$ Needles; melting-point, 225°.

3 mol. HCl + water ….. $c = 2$ (anhydrous), $[\alpha]_D^{15} = -140°$ [6]

β-CINCHONIDINE, $C_{19}H_{22}N_2O$. Crystals, melting-poi 206° to 207°.

3 mol HCl + water…… . . $c = 1.25$, $[\alpha]_D^{15} = -181.4°$ [7]

Melting-point, 244°.

Alcohol ($d = 0.7944$)… …. $c = 0.5$, $[\alpha]_D^{20} = -171.5°$ [8]

γ-CINCHONIDINE, $C_{19}H_{22}N_2O$. Crystals, melting-point, 238

Alcohol ($d = 0.7944$)……… $c = 0.5$, $[\alpha]_D^{20} = -164.6°$ [9]

APOCINCHONIDINE, $C_{19}H_{22}N_2O$ Thin plates, melting-poi 225° (turns brown).

Alcohol (97 vol. p c) $c = 0.8$, $[\alpha]_D^{15} = -129.2°$
3 mol HCl + water… $c = 2$ " $= -160.4$ (from cinchonidine)
3 " " + " .. $c = 2$, " $= -160.2$ (from homocinchonidine)

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[1] Hesse Ann Chem (Liebig), **176**, 222
[2] *Ibid*, **182**, 51
[3] Rec trav chim Pays-Bas, **1**, 18
[4] Ann chim phys [7], **1**, 5
[5] Hesse Ann. Chem (Liebig), **205**, 319
[6] Hesse *Ibid*, **267**, 142
[7] Hesse *Ibid*, **205**, 328 (note)
[8] Neumann Wien Monatsh. Chem, **13**, 660
[9] Neumann
[10] Hesse Ann Chem (Liebig), **205**, 329

Acetylapocinchonidine, $C_{19}H_{21}(C_2H_3O)N_2O$. Crystals.

Alcohol (97 vol p. c) .... $c = 2$, $[\alpha]^{15}_{D} = -61.8°$ } [1]
3 mol HCl + water............ $c = 2$, " $= -87.9$ }

Chlorapocinchonidine, $C_{19}H_{23}ClN_2O$. Thin plates; melting-point, 200°

3 mol. HCl + water .... $c = 2$, $[\alpha]^{15}_{D} = -142.2°$ [2]

Left-rotating in alcohol solution, also.

Acetylchlorapocinchonidine, $C_{19}H_{22}(C_2H_3O)ClN_2O$. Prisms; melting-point, 150°.

3 mol. HCl + water............. $c = 2$, $[\alpha]^{15}_{D} = -54\ 3°$ [3]

HOMOCINCHONIDINE. Skraup,[4] also Claus and Weller,[5] consider this alkaloid as identical with cinchonidine, $C_{19}H_{22}N_2O$. Melting-point, 205° to 206°

Alcohol (97 vol p. c)........ $c = 2$, $[\alpha]^{15}_{D} = -109.3°$ [6]
" " .... $c = 2$, " $= -107\ 3$ } [7]
Chloroform .. . . $c = 4$, " $= -70\ 0$ }
3 mol HCl + water ... . $c = 5$, " $= -167.9$ }

Hydrochloride, $C_{12}H_{22}N_2O.HCl + H_2O$. Rhombic octahedra.

2 mol HCl + water . ... $c = 10$, $[\alpha]^{20}_{D} = -139\ 0°$ [8]

Sulphate, $(C_{19}H_{22}N_2O)_2.H_2SO_4 + 6H_2O$ Prisms

Two grams of the anhydrous salt are dissolved in 20 cc of normal hydrochloric acid and diluted to 25 cc. with water.

$c = 8$ (anhydrous), $[\alpha]^{15}_{D} = -137\ 96°$ [9]

Acetylhomocinchonidine, $C_{19}H_{21}(C_2H_3O)N_2O$. Brittle mass; melting-point, 42°.

Alcohol (97 vol p c.) .. .. $c = 2$, $[\alpha]^{15}_{D} = -34\ 0°$ } [9]
1 mol HCl + water............. $c = 2$, " $= -61\ 1$ }
3 " " + " ... . $c = 2$, " $= -72.5$ }

CINCHOLEUPONIC ACID, $C_8H_{13}NO_4 + H_2O$. Crystals, melt-

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[1] Hesse *Loc cit*, p 338

[2] Hesse *Loc cit*, p 346

[3] Hesse *Loc cit*, p 353

[4] Ber d. chem Ges, **13**, Ref. 933

[5] *Ibid*, **14**, 1921

[6] Hesse *Ibid*, **10**, 2156

[7] Hesse Ann Chem (Liebig), **205**, 203

[8] Hesse Ber d chem Ges., **14**, 1891

[9] Hesse Ann Chem (Liebig), **205**, 320

ing-point, 126° to 127° (hydrated); 225° to 226°[1] (anhydro
221° to 222°[2] (anhydrous).

Made by oxidation of .

Cinchonine	Water,	$c = 4$,	$[\alpha]_D^{20} = +30.00°$ [3]
Chitenine	"	$c = 4$,	" $= +30.25$
Cinchonidine	"	$c = 4$,	" $= +30.17$ [4]
Quinidine	"	$c = 4$,	" $= +30.9$ [5]

Hydrochloride, $C_8H_{13}NO_4.HCl$ Triclinic prisms; melti
point, 193° to 194°.

Made from .

Cinchonine .	Water,	$c = 4$,	$t = 20°$,	$[\alpha]_D = +37.75°$ [3]
Chitenine. . .	"	$c = 4$,	$t = 23$	" $= +34.0$
Cinchonidine ..	"	$c = 4$,	$t = 20$	" $= +40.2$ [4]
Quinidine	"	$c = 4$,	$t = 20$	" $= +39.6$ [6]
Cinchonicine ..	"	$c = 4$,	$t = 20$	" $= +35.6$ [7]
Quinicine	"	$c = 4$,	$t = 20$	" $= +35.6$

ARICINE, $C_{23}H_{26}N_2O_4$ Crystals; melting-point, 188°.

Ether ($d = 0.72$)	$c = 1$ to 2.5,	$[\alpha]_D^{15} = -94.7°$ [8]
Alcohol (97 vol. p. c.) ...	$c = 1$,	" $= -54.1$

No rotation in hydrochloric acid solution

CUSCONINE, $C_{23}H_{26}N_2O_4 + 2H_2O$ Crystals, melting-poi
110°

Ether ($d = 0.72$)	$c = 1$,	$[\alpha]_D^{15} = -27.1°$ [9]
" "	$c = 2$,	" $= -26.8$
Alcohol (97 vol. p. c.)	$c = 2$,	" $= -54.3$
3 mol HCl + water...	$c = 0.5$,	" $= -71.8$

CONCUSCONINE, $C_{23}H_{26}N_2O_4 + H_2O$. Monoclinic crystal
melts at 144°, then solidifies and melts again at 206° to 20

Alcohol (97 vol. p. c.)	$c = 2$,	$[\alpha]_D^{15} = +36.8°$ [10]
" "	$c = 2$,	" $= +40.8°$ [11]

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[1] Skraup Monatsh Chem., 10, 46

[2] Schniderschitsch Wien Monatsh Chem., 10, 60

[3] Skraup

[4] Schniderschitsch

[5] Wurstl Wien. Monatsh Chem., 10, 70

[6] Würstl

[7] Skraup, Wurstl Wien Monatsh Chem., 10, 226

[8] Hesse Ann Chem (Liebig), 185, 313.

[9] Hesse *Ibid.*, 185, 303, Ber d. chem Ges., 16, 61

[10] Hesse Ber d chem Ges., 16, 61

[11] Hesse Ann Chem (Liebig), 225, 236

α-Concusconinemethylsulphate, $(C_{23}H_{26}N_2O_4.CH_3)_2.SO_4$ (at 120°) Amorphous.

Water	$c = 3.764$ (anhydrous),	$[\alpha]_D^{15} = +73°$

β-Concusconinemethylsulphate, $(C_{23}H_{26}N_2O_4.CH_3)_2.SO_4$ (at 120°)

A 2 per cent. aqueous solution was optically inactive.[1]

QUINAMINE, $C_{19}H_{24}N_2O_2$. Long prisms; melting-point, 172°.

Alcohol (96 (?) vol. p. c.)	$c = 0.8378$,	$[\alpha]_D^{15} = +106.8°$ [2]
Alcohol (97 vol. p. c.)	$c = 2$,	$[\alpha]_D^{15} = +104.5°$ [3]
1 mol. HCl + water	$c = 2$,	" $= +116.0$
3 " " + "	$c = 2$,	" $= +117.2$
Chloroform	$c = 2$,	$[\alpha]_D^{15} = +93.50°$ [4]
Absolute alcohol	$c = 0.502$,	$[\alpha]_D^{15} = +104.6°$ [5]
" "	$c = 1.016$,	" $= +103.9$
" "	$c = 1.494$,	" $= +102.8$
" "	$c = 1.774$,	" $= +100.7$
Alcohol (90 wt. p. c.)	$c = 1.648$,	" $= +101.5$
Absolute ether	$c = 0.458$,	" $= +121.4$
" "	$c = 1.024$,	" $= +119.9$
Chloroform	$c = 0.722$,	" $= +94.9$
"	$c = 1.512$,	" $= +94.0$
"	$c = 2.235$,	" $= +93.3$
Benzene	$c = 0.056$,	" $= +99.3$
"	$c = 1.489$,	" $= +100.9$

The influence of acids (HCl, HNO_3, $HClO_3$, $HC_2H_3O_2$, $HCHO_2$, H_2SO_4, $H_2C_2O_4$, H_3PO_4) on the specific rotation is discussed in these papers.

Hydrochloride, $C_{19}H_{24}N_2O_2.HCl + H_2O$. Prisms.

Alcohol (97 vol. p. c.)	$c = 2$,	$[\alpha]_D^{15} = +118.1°$ [3]
Water	$c = 2$,	" $= +100.0$

Hydrobromide, $C_{19}H_{24}N_2O_2.HBr + H_2O$. Prisms.

Water	$c = 4$,	$[\alpha]_D^{15} = +88.2°$ [6]

Hydroiodide, $C_{19}H_{24}N_2O_2.HI$ Crystals.

Absolute alcohol	$c = 1.068$,	$[\alpha]_D^{16} = +92.5°$ [7]
" "	$c = 1.644$,	" $= +94.4$
" "	$c = 2.310$,	" $= +95.8$

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[1] Hesse Ann. Chem. (Liebig), **225**, 241

[2] Hesse *Ibid.*, **166**, 272.

[3] Hesse *Ibid.*, **207**, 307

[4] Hesse *Ibid.*, **199**, 337

[5] Oudemans, *Ibid.*, **197**, 54, Rec. trav. chim. Pays-Bas, **1**, 22 to 24

[6] Hesse *Loc. cit.*

[7] Oudemans Ann. Chem. (Liebig), **197**, 60

Nitrate, $C_{19}H_{24}N_2O_2\ HNO_3$. Monoclinic crystals.

Water................ $c = 0\ 997$, $[\alpha]_D^{16} = +\ 96\ 8°$ [1]
" .... $c = 1\ 934$, " $= +\ 97.0$
Absolute alcohol...... $c = 0\ 9945$, " $= +\ 109.2$
" " ...... $c = 2.036$, " $= +\ 109\ 6$

Perchlorate, $C_{19}H_{24}N_2O_2\ HClO_4$. Anhydrous crystals.

Absolute alcohol...... $c = 0\ 709$, $[\alpha]_D^{16} = +\ 99.3°$ [2]
" " ..... $c = 2\ 1335$, " $= +\ 101\ 8$

QUINAMIDINE, $C_{19}H_{24}N_2O_2$ Wart-like bunches; meltin point, 93° (not corr.).

Alcohol (97 vol p c.)........... $c = 2$, $[\alpha]_D^{15} = +\ 4\ 5°$ [3]

Hydrochloride, $C_{19}H_{24}N_2O_2.HCl + H_2O$. Prisms.

Inactive in 2 per cent. aqueous solution.[4]

QUINAMICINE, $C_{19}H_{24}N_2O_2$ Crystals; melting-point, 10 (uncorr.)

Alcohol (97 vol. p. c)...... $c = 2$, $[\alpha]_D^{15} = +\ 38.1°$ [4]
3 mol. HCl + water.... ... $c = 2$, " $= +\ 47\ 0$

APOQUINAMINE, $C_{19}H_{22}N_2O$(at 100°) Crystals, meltin point, 114° (uncorr).

Inactive in 2 per cent. alcoholic solution.

1.1 mol HCl + water...... $c = 2$, $[\alpha]_D^{15} = -\ 28\ 4°$ [4]
3 " " + " ...... $c = 2$, " $= -\ 29\ 1$
10 " " + " ...... $c = 2$, " $= -\ 30.0$

Acetylapoquinamine, $C_{19}H_{21}(C_2H_3O)N_2O$ (at 100°). Amo phous.

Alcohol (97 vol p c.)...... $c = 2$, $[\alpha]_D^{15} = 0°$ [4]
10 mol. HCl + water ...... $c = 2$, " $= -\ 31\ 2$

HYDROCINCHONIDINE, $C_{19}H_{24}N_2O$, according to Forst an Boehringer,[5] is identical with Hesse's cinchamidine. Crystals melting-point, 229°;[6] 230°.[7]

Alcohol (97 vol p. c)......... $c = 2$, $[\alpha]_D^{15} = -\ 98.4°$ [8]

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[1] Oudemans *Loc cit*, p 58

[2] Oudemans *Loc cit*, p 59

[3] Hesse Ann Chem (Liebig), **207**, 307

[4] Hesse *Loc cit*

[5] Ber. d chem. Ges, **15**, 520

[6] Forst, Boehringer

[7] Hesse

[8] Hesse Ber d chem Ges, **14**, 1683

The specific rotation is greater in acid solution.

On fusing the acid sulphate, an amorphous modification of hydrocinchonidine is formed, which melts below 100°.

3 mol. HCl + water.............. $c = 2$, $[\alpha]_D^{15} = -12°$ [1]

Hydrochloride, $C_{19}H_{24}N_2O.HCl + 2H_2O$. Prisms.

Water......................	$c = 2$,	$[\alpha]_D^{15}$	$-80.4°$ [2]
"	$c = 5$,	"	-66.0
"	$c = 8$,	"	-60.4
2 mol. HCl + water........	$c = 5$,	"	-109.4
Alcohol (97 vol. p. c.)......	$c = 5$,	"	-72.4

Neutral Sulphate, $(C_{19}H_{24}N_2O)_2.H_2SO_4 + 7H_2O$. Needles.

Water...................	$c = 2$,	$[\alpha]_D^{15}$	$-75.2°$ [3]
Alcohol (97 vol. p. c.)..	$c = 2$,	"	-93.8

Acid Sulphate, $C_{19}H_{24}N_2O.H_2SO_4 + 4H_2O$. Prisms.

Water .... $c = 4$, $[\alpha]_D^{15} = -92.7°$ [3]

Acetylhydrocinchonidine, $C_{19}H_{23}N_2O.C_2H_3O$. Amorphous; melting-point, 42°.

Alcohol (97 vol. p. c.)......	$c = 2$,	$[\alpha]_D^{15}$	$-29.5°$ [3]
3 mol. HCl + water........	$c = 2$,	$[\alpha]_D^{15}$	-50.9

CONQUINAMINE, $C_{19}H_{24}N_2O_2$. Triclinic crystals; melting-point, 123° (corr.).

Alcohol (97 vol. p. c.)......	$c = 2$,	$[\alpha]_D^{15}$	$+204.6°$ [4]
Chloroform...............	$c = 2$,	"	$+184.5$
1 mol. HCl + water......	$c = 2$,	"	$+229.1$
3 " " + "	$c = 2$,	"	$+230.0$
3 " " + "	$c = 4$,	"	$+230.0$

Absolute alcohol....................	$c = 0.8025$,	$[\alpha]_D^{15}$	$+205.1°$ [5]
" "	$c = 0.8195$,	"	$+204.2$
" "	$c = 1.531$,	"	$+203.5$
" "	$c = 2.7115$,	"	$+202.6$
" "	$c = 3.154$,	"	$+203.0$
" "	$c = 4.018$,	"	$+204.1$
" "	$c = 4.986$,	"	$+203.5$
Alcohol (91 wt. p. c.)...............	$c = 1.7595$,	"	$+204.3$
" (80 wt. p. c.)...............	$c = 1.813$,	"	$+205.5$
Absolute ether......................	$c = 0.7655$,	"	$+192.7$
" "	$c = 1.1515$,	"	$+190.6$
" "	$c = 1.522$,	"	$+188.1$

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[1] Hesse: Ann. Chem. (Liebig), **214**, 1.

[2] Hesse: *Loc. cit.*

[3] Hesse.

[4] Hesse: Ann. Chem. (Liebig), **209**, 68.

[5] Oudemans: *Ibid.*, **209**, 46; Rec. trav. chim. Pays-Bas, **1**, 23 to 25.

Absolute ether .... $c = 1.6155$, $[\alpha]^{15}_D = + 189.0°$
" " .... $c = 3.052$, " $= + 190.7$
" " .... $c = 3.0585$, " $= + 190.5$
" " .... $c = 4.6465$, " $= + 190.3$
Chloroform .... $c = 0.7945$, " $= + 176.1$
" .... $c = 1.531$, " $= + 173.8$
" .... $c = 3.050$, " $= + 171.2$
Benzene .... $c = 0.8955$, " $= + 180.1$
" .... $c = 1.540$, " $= + 179.1$
" .... $c = 2.1285$, " $= + 178.6$
" .... $c = 3.028$, " $= + 178.2$
" .... $c = 3.477$, " $= + 178.0$

The influence of different acids on the specific rotation of conquinamine is discussed in the same papers

Hydrochloride, $C_{19}H_{24}N_2O_2.HCl$. Octahedral crystals.

Water .... $c = 4$, $[\alpha]^{15}_D = + 205.3°$ [2]
Alcohol (97 vol p c) .. $c = 4$, " $= + 206.4$

Hydrobromide, $C_{19}H_{24}N_2O_2$ HBr. Monoclinic crystals.

Absol. alcohol, $c = 1.162$, $[\alpha]^{16}_D = + 182.7°$; alkaloid, $[\alpha]^{16}_D = + 230$
" " $c = 1.9935$, " $= + 181.0$, " " $= + 228$

Hydroiodide, $C_{12}H_{24}N_2O_2.HI$. Crystals.

Absol. alcohol, $c = 1.011$, $[\alpha]^{16}_D = + 162.8°$, alkaloid, $[\alpha]^{16}_D = + 229$
" " $c = 2.213$, " $= + 162.2$, " " $= + 229$

Nitrate, $C_{19}H_{24}N_2O_2.HNO_3$. Rhombic crystals.

Absol alcohol, $c = 1.2685$, $[\alpha]^{16}_D = + 190.0°$, alkaloid, $[\alpha]^{16}_D = + 228$

Chlorate, $C_{19}H_{24}N_2O_2.HClO_3$. Monoclinic needles.

Absol alcohol, $c = 0.915$, $[\alpha]^{16}_D = + 184.0°$, alkaloid, $[\alpha]^{16}_D = + 234.0$

Perchlorate, $C_{19}H_{24}N_2O_2.HClO_4$. Monoclinic needles.

Absol alcohol, $c = 0.710$, $[\alpha]^{16}_D = + 175.4°$; alkaloid, $[\alpha]^{16}_D = + 231.8$
" " $c = 1.4755$, " $= + 175.0$, " " $= + 231.4$

Formate, $C_{19}H_{24}N_2O_2.CH_2O_2$ Monoclinic crystals.

Absol alcohol, $c = 0.884$, $[\alpha]^{16}_D = + 195.8°$; alkaloid, $[\alpha]^{16}_D = + 224.7$
" " $c = 1.785$, " $= + 193.0$, " " $= + 222.6$

Acetate, $C_{19}H_{24}N_2O_2.C_2H_4O_2$ Tetragonal crystals.

Absol. alcohol, $c = 0.921$, $[\alpha]^{16}_D = + 181.0°$, alkaloid, $[\alpha]^{16}_D = + 215.8$
" " $c = 0.8395$, " $= + 179.0$, " " $= + 213.5$

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[1] Oudemans Ann Chem (Liebig), **209**, 46, Rec trav chim Pays-Bas, **1**, 23 to 25

[2] Hesse Ann Chem (Liebig), **209**, 68

Oxalate, $C_{19}H_{24}N_2O.C_2H_2O_4 + 3H_2O$. Rhombic crystals; melting-point, about 115°.

Absol. alcohol, $c = 1.0315$, $[\alpha]_D^{16} = +163.0°$; alkaloid, $[\alpha]_D^{16} = +200.6°$
" " $c = 1.525$, " $= +162.6$; " " $= +200.6$

HYDROQUININE, $C_{20}H_{26}N_2O_2 + 2H_2O$. Crystals; melting-point, 172.3° (corr.).

Chloroform-alcohol mixture.... $c = 2.49$, $[\alpha]_D^{17.8} = -160.25°$[1]

Melting-point, 168°.

Alcohol (95 vol. p. c.) .... $c = 2.4$, $[\alpha]_D^{20} = -142.2°$

In 100 cc., 40 cc. of normal HCl:

$c = 2.4$, $[\alpha]_D^{20} = -227.1°$[2]

Neutral Sulphate, $(C_{20}H_{26}N_2O_2)_2H_2SO_4 + 6$ or $8H_2O$. Colorless needles.

4 mol. HCl | water........... $c = 4$ (anhydrous), $[\alpha]_D^{15} = -222.5°$[3]
4 " " | " .... $c = 4$ " " $= -193.4°$ }[4]
4 alkaloid, " $= -255.9°$ }

Acetyl Hydroquinine, $C_{20}H_{25}N_2O_2(C_2H_3O)$. Varnish-like mass; melting-point, about 40°.

3 mol. HCl | water......... $c = 3$, $[\alpha]_D^{15} = -73.9°$[5]

HYDROQUINICINE, $C_{20}H_{26}N_2O_2$. Yellowish varnish

3 mol HCl | water .... $c = 3$, $[\alpha]_D^{15}$ 17°[6]

DICINCHONINE, $C_{19}H_{22}N_2O$[7] Amorphous; melting-point, 40°.

Alcohol (97 vol. p. c.). .... $c = 1.516$, $[\alpha]_D^{15} = +91.7°$
3 mol. HCl | water........ $c = 1$, " $+80.4°$

Hydrochloride, $C_{19}H_{22}N_2O$ HCl. Prisms

Water .... $c = 5$, $[\alpha]_D^{15} = +58.7°$[8]

PARICINE, $C_{16}H_{18}N_2O + 1^1/_2H_2O$ Yellow powder; melting-point, 130°. The alcoholic solution is inactive.[9]

GEISSOSPERMINE, $C_{19}H_{24}N_2O_2 + H_2O$. Small prisms, melting-point, 160°, with decomposition.

Alcohol (97 vol. p. c.). .... $c = 1.5$ (anhydrous), $[\alpha]_D^{15} = -93.4°$[10]

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[1] Lenz: Ztschr. anal. Chem., **27**, 561

[2] Hesse: Ann. Chem. (Liebig), **241**, 259

[3] Hesse: Ber. d. chem. Ges, **15**, 856.

[4] Hesse. Ann Chem. (Liebig), **241**, 262.

[5] Hesse. *Loc. cit.*, p. 278.

[6] Hesse · *Loc. cit.*, p. 274

[7] Hesse: Ann. Chem (Liebig), **276**, 119.

[8] Hesse: *Ibid.*, **227**, 153.

[9] Hesse · *Ibid.*, **166**, 263.

[10] Hesse, Ber. d. chem. Ges, **10**, 2164.

CINCHONAMINE, $C_{19}H_{24}N_2O$ Glistening needles; melting point, 184° to 185°.

Alcohol (97 vol. p. c.)......... $c = 2$, $[\alpha]^{15}_{D} = +121.1°$ [1]

According to Arnaud,[2] $[\alpha]_D = +117.9°$ in alcoholic solution (93 per cent.). Melting-point, 195°.

Neutral Sulphate, $(C_{19}H_{24}N_2O)_2.H_2SO_4$. Prisms.

Water............... $c = 2$, $[\alpha]^{15}_{D} = +36.7°$ [3]
" .... $c = 6$, " $= +39.8$
1 mol. H_2SO_4 + water... $c = 2$, " $= +39.6$
2 " " + " .. $c = 2$, " $= +35.7$ [4]
1 " " + " .. $c = 3$, " $= +43.5$ [5]

Acid Sulphate, $C_{19}H_{24}N_2O\ H_2SO_4$. Prisms.

Water.......... $c = 2$, $[\alpha]^{15}_{D} = +34.9°$ [6]
" .... $c = 6$, " $= +37.4$

CHAIRAMINE, $C_{22}H_{26}N_2O_4 + H_2O$. Crystals; melting-point, 233°.

$[\alpha]_D$ = about +100° [7]

CONCHAIRAMINE, $C_{22}H_{26}N_2O_4 + H_2O + C_2H_6O$ (from alcohol) Prisms; melting-point, 82° to 86°; 120° (anhydrous).

Alcohol (97 vol. p. c.), $c = 2$, (alcohol and water-free), $[\alpha]^{15}_{D} = +68.4°$ [8]

CHAIRAMIDINE, $C_{22}H_{26}N_2O_4 + H_2O$. Amorphous, melting-point, 126° to 128°.

Alcohol (97 vol. p. c.)........ $c = 3$ (anhydrous), $[\alpha]^{15}_{D} = +7.3°$ [9]

CONCHAIRAMIDINE, $C_{22}H_{26}N_2O_4 + H_2O$. Crystals; melting-point, 114° to 115°

Alcohol (97 vol. p. c.).......... $c = 3$ (anhydrous), $[\alpha]^{15}_{D} = -60°$ [10]

Alkaloids of Coca Leaves

d-ECGONINE, $C_9H_{15}NO_3$. Crystals; melting-point, 254°.

The constitutional formula of Einhorn and Tahara[11] contains three asymmetric carbon atoms (compare Einhorn[1]), while that of Merling[2] has four such atoms.

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[1] Hesse Ann Chem (Liebig), **225**, 220
[2] Compt rend, **93**, 593
[3] Hesse *Loc cit*, p. 224
[4] Hesse Ber d chem Ges, **16**, 62
[5] Arnaud. Compt rend, **97**, 174
[6] Hesse. *Loc. cit.*
[7] Hesse
[8] Hesse *Loc cit.*, p 248
[9] Hesse *Loc cit*, p 254
[10] Hesse *Loc cit*, p 256
[11] Ber d chem Ges, **26**, 324

Hydrochloride, $C_9H_{15}NO_3.HCl$. Monoclinic hemimorphous crystals.

Water............ $p = 4.4$, $[\alpha]_D^{20} = +18.2°$ [3]

Methyl Ester, $C_9H_{14}NO_3.CH_3$. Prismatic crystals; melting-point, 115°.

Dilute alcohol............ $p = 6.22$, $[\alpha]_D^{20} = +22.5°$ } [4]
" " .... $p = 6.25$, " $= +22.4$ }

Isovaleryl-d-Ecgonine Methyl Ester Hydrochloride, C_5H_9O $C_9H_{14}NO_3.CH_3.HCl$. Thin leaves; melting-point, 192°.

Alcohol .... $c = 2.01$, $[\alpha]_D^{20} = +25.4°$ [5]

Cinnamyl-d-Ecgonine Methyl Ester Hydrochloride, C_9H_7O $C_9H_{14}NO_3.CH_3.HCl$. Needles; melting-point, 186° to 188°.

Alcohol .... $c = 2.11$, $[\alpha]_D^{20} = +47.4°$ [6]

Derivatives of Benzoyl-d-Ecgonine

Methyl Ester (*d*-Cocaine). Constitution · Einhorn,[7] two asymmetric C atoms; Einhorn, Tahara,[8] three asymmetric C atoms, $C_5H_7N.CH_3.CH_3.CHO(CO.C_6H_5)CH_2.COOCH_3$.

Hydrochloride, $C_{17}H_{21}NO_4HCl$. Monoclinic plates; melting-point, 205°.

Alcohol ($d_4^{20} = 0.9353$)....... $c = 1.9$, $[\alpha]_D^{20} = +39.47°$ [9]

Ethyl Ester Hydrochloride, $C_{18}H_{23}NO_4.HCl + H_2O$. Plates, melting-point, 215°.

Water .... $c = 2$, $[\alpha]_D^{20} = +40°$

Propyl Ester Hydrochloride, $C_{19}H_{25}NO_4.HCl + H_2O$. Prisms; melting-point, 220°.

Water .... $c = 2.6$, $[\alpha]_D^{20} = +46.2°$

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[1] Ber. d. chem. Ges., **22**, 1495

[2] *Ibid.*, **24**, 3116.

[3] Einhorn, Marquardt, Koch · *Ibid.*, **23**, 468

[4] Liebermann, Giesel: *Ibid.*, **23**, 926

[5] Deckers, Einhorn: *Ibid.*, **24**, 7.

[6] Deckers, Einhorn.

[7] Ber. d. chem. Ges., **21**, 3029.

[8] *Ibid.*, **26**, 324

[9] Einhorn, Marquardt: *Ibid.*, **23**, 468.

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Butyl Ester Hydrochloride, $C_{20}H_{27}NO_4.HCl + H_2O$. Fine matted needles; melting-point, 201°.

Water .... c 2.5, $[\alpha]_D$ + 46°

Amyl Ester Hydrochloride, $C_{21}H_{29}NO_4.HCl$. Fine matted needles; melting-point, 217°.

Water .... c 2.2, $[\alpha]_D$ + 38.6°[1]

l-ECGONINE HYDROCHLORIDE, $C_9H_{15}NO_3.HCl$. Triclinic plates; melting-point, 246°.

Water........... $[\alpha]_D$ 57°[2]

Cinnamyl-l-ecgonine Methyl Ester, $C_9H_7O.C_8H_{13}NO_3.CH_3$. Crystals; melting-point, 121°.

Chloroform .... c 10, $[\alpha]_D^{15}$ 4.7°[3]

Hydrochloride, $C_{19}H_{23}NO_4.HCl + 2H_2O$. Crystals; melting point, 176°.

Water.......... c 66 (anhydrous), $[\alpha]_D^{15}$ 104.1°[4]

Benzoyl-l-ecgonine Methyl Ester (*l*-Cocaine ordinary cocaine), $C_5H_7N.CH_3.CHO(CO.C_6H_5)CH_2.COOCH_3$. Monoclinic prisms; melting-point, 98°.

Chloroform .... $p = 10$ to 20, $[\alpha]_D^{20} = -16.412 + 0.00585\,p$,

from the following observations:

p	d_4^{20}.	$[\alpha]_D^{20}$.	
		Found	Calculated
9.925	1.4480	-16.356	-16.354[5]
25.484	1.3971	16.280	16.263
15.643	1.4293	-16.319	-16.320
18.793	1.4190	16.299	-16.302
20.242	1.4126	-16.283	-16.293

The specific rotation is, therefore, almost constant.

Hydrochloride, $C_{17}H_{21}NO_4.HCl$. Crystals; melting-point, 181.5°.[6] Five preparations from different factories, when dissolved in alcohol ($d_4^{20} = 0.9353 = 40$ per cent. weight), showed specific rotations at $t = 20°$, and for concentrations between $c = 5$ and 25 which may be expressed by the following formulas:

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[1] Einhorn, Marquardt: Ber. d. chem. Ges., **23**, 986-988

[2] Einhorn: *Ibid.*, **22**, 1495.

[3] Hesse: Ann. Chem. (Liebig), **271**, 185.

[4] Hesse. *Loc. cit.*

[5] Antrick: Ber. d. chem Ges., **20**, 321.

[6] Antrick.

Preparation I m. p. 181.5°, $[\alpha]_D^{20} = -67.904 + 0.15654\,c$
" II " 182.5, " $-68.023 + 0.15898\,c$
" III " 185, " $= -69.769 + 0.174407\,c$
" IV " 184, " $-67.951 + 0.15458\,c$
" V " 181.5 " $= -68.052 + 0.163\,c$

from which, in the mean,

$$[\alpha]_D^{20} = -67.982 + 0.15827\,c\ ^{1}$$

On the polarimetric determination of cocaine, see § 186, p. 501.

Isatropyl Cocaine, $C_{19}H_{23}NO_4$ (at 45°). Amorphous.

Alcohol .... $c = 4$, $[\alpha]_D^{20} = -29.3°$ [2]

ANHYDROECGONINE is formed from *d*- as well as from *l*-ecgonine.

Hydrochloride, $C_9H_{13}NO_2.HCl + H_2O$. Rhombic hemimorphous crystals; melting-point, 240° to 241°

Water .. .. $[\alpha]_D = -61.5°$ [3]

Melting-point, 238° to 240°

Water, $c = 3$ (anhydrous) .. $[\alpha]_D^{20} = -62.7°$ [4]

l-ECGONINIC ACID, $C_7H_{11}NO_3$. From *d*- and *l*-ecgonine Crystals; melting-point, 117°.

Water .... $c = 12.37$, $[\alpha]_D^{20}$ 43.2° [5]

d-TROPINIC ACID, $C_6H_{11}N(COOH)_2$. Crystals, melting-point, 247° to 248°.

Water .... $p = 11.76$, $d = 1.036$, $[\alpha]_D^{20} = +14.8°$ [6]

Alkaloids of Opium

MORPHINE, $C_{17}H_{17}(OH)_2NO + H_2O$. Small rhombic columns.

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[1] Antrick: Ber. d. chem. Ges., **20**, 310.
[2] Liebermann: *Ibid.*, **21**, 2342.
[3] Einhorn: *Ibid.*, **22**, 1495.
[4] Hesse: Ann. Chem. (Liebig), **271**, 180.
[5] Liebermann: Ber. d. chem. Ges., **24**, 612.
[6] Liebermann, p. 611.

1 mol. alkaloid + 1 mol Na_2O .... $c = 2$, $[\alpha]_D^{22.5} = -67.5°$ [1]
1 " " + 5 " " .... $c = 2$, " $= -70.2$
1 " " + 2 " " .... $c = 5$, " $= -71.0$
Absolute alcohol.. .... $c = 1.00$ to 1.80, $[\alpha]_D^{20} = -140.5°$ [2]

Hydrochloride, $C_{17}H_{19}NO_3\,HCl + 3H_2O$. Crystals.
Water .... $c = 1$ to 4, $[\alpha]_D^{15} = -100.67 + 1.14c$ [3]
10 mol HCl + water......... $c = 2$, " $= -94.3°$

Sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$. Crystals.
Water... .. .. . $c = 1$ to 4, $[\alpha]_D^{15} = -100.47 + 0.96c$ [3]

Acetate, $C_{17}H_{19}NO_3\,C_2H_4O_2 + 3H_2O$. Crystals
Absolute alcohol. .. .. $c = 1.2$, $[\alpha]_D = -100.4°$ [4]
Alcohol ($d = 0.865$)....... $c = 0.97$, " $= -98.9$
Water.. .. .. $c = 2.5$, " $= -77$
" .... $c = 0.996$, " $= -72$

The effect of acids (HCl, HNO_3, $HCHO_2$, $HC_2H_3O_2$, H_2SO_4, $H_2C_2O_4$, H_3PO_4, H_3AsO_4, $C_6H_8O_7$) on the rotation of morphine has been investigated by Tykociner[5]

CODEINE (Morphine methyl ether), $C_{17}H_{17}(OCH_3)(OH)NO + H_2O$ Rhombic crystals; melting-point, 155°,[6] 153°[7]

Alcohol (97 vol. p. c.) $c = 2$ to 8, $[\alpha]_D^{15} = -135.8°$ [8]
" (80 " ") $c = 2$, " $= -137.8$
Chloroform .... $c = 2$, " $= -111.5$
Absolute alcohol.... .. .... $c = 2.32$ (anhydrous), $[\alpha]_D^{20} = -134.3°$ [2]
" " .... $c = 2.97$ " " $= -141.1$
Alcohol.... .... $c = 4.1$, $[\alpha]_D = -130.34°$ [9]
Commercial codeine, alcohol, $c = 4.1$ " $= -133.18°$

Hydrochloride, $C_{18}H_{21}NO_3\,HCl + 2H_2O$ Short needles.
Water...................... $c = 2$, $[\alpha]_D^{22.5} = -108.2°$ [3]
10 mol HCl + water....... $c = 2$, " $= -105.2$
Alcohol (80 vol. p. c.).. ... $c = 2$, " $= -108$

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[1] Hesse Ann Chem. (Liebig), **176**, 190
[2] Tykociner Rec trav chim Pays-Bas, **1**, 147
[3] Hesse *Loc. cit*
[4] Oudemans Ann Chem (Liebig), **166**, 77
[5] *Loc cit*
[6] Hesse Ann Chem (Liebig), **222**, 210
[7] Grimaux, Compt rend, **92**, 1228
[8] Hesse. Ann Chem (Liebig), **176**, 191
[9] Grimaux *Loc cit.*

Sulphate, $(C_{18}H_{21}NO_3)_2.H_2SO_4 + 5H_2O$. Rhombic prisms.

Water .... c = 3, $[\alpha]_D^{15}$ = − 101.2° } [1]
" .. .. c = 3, $[\alpha]_D^{25}$ = − 100.9 }

The influence of acids on the specific rotation of codeine has been investigated by Tykociner;[2] in the neutral salts, $[\alpha]_D^{20}$ = about − 134° (compare morphine).

Methylcodeine Sulphate, $(C_{17}H_{18}(CH_3)NO_3.CH_3)_2SO_4 + 4H_2O$. Rhombic crystals.

Water .... c = 5 (hydrated), $[\alpha]_D^{15}$ = − 130.1° [3]

Methocodeine (Morphine dimethyl ester), $C_{17}H_{17}(OCH_3)_2.NO$. Crystals; melting-point, 118.5°.

Alcohol (97 vol. p. c.).. ...... c = 4, $[\alpha]_D^{15}$ = − 208.6° [4]

α-Methocodeine (α-Methylmorphimethine). Melting-point, 118.5°.

Ether .... c = 2.13, $[\alpha]_D^{17}$ = − 212°

Methiodide. Melting-point, 245°

Alcohol .... c = 1.4, $[\alpha]_D^{17}$ = − 94.56°

Acetyl Derivative. Melting-point, 66°.

Alcohol .... c = 2.698, $[\alpha]_D$ = − 96.3°

Acetyl Methiodide. Melting-point, 207°.

Alcohol .... c = 0.586, $[\alpha]_D$ = − 73.87°

β-Methylmorphimethine (does not crystallize).

Ether .... c = 3.746, $[\alpha]_D^{17}$ = + 437.3°

Methiodide. Melting-point, 297°.

Alcohol .... c = 1.248, $[\alpha]_D$ = + 227.45°

Acetyl Derivative (does not crystallize).

Alcohol .... c = 0.798, $[\alpha]_D$ = + 413.9°

Acetyl Methiodide. Amorphous.

Alcohol .... c = 0.59, $[\alpha]_D$ = + 257.6° [5]

PSEUDOCODEINE, $C_{18}H_{21}NO_3 + H_2O$. Needles; melting-point, 178° to 180°.

Alcohol .... p = 1.91, $[\alpha]_D$ = − 91.1° [6]

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[1] Hesse: *Loc. cit.*

[2] *Loc. cit.*

[3] Hesse: Ann Chem (Liebig), **222**, 215

[4] Hesse: *Loc. cit.*, p. 218.

[5] Knorr: Ber. d. chem. Ges., **27**, 1144

[6] Merck: Arch. Pharm., **229**, 161.

THEBAINE, $C_{17}H_{15}NO(OCH_3)_2$. Crystals; melting-point, 103°

Alcohol (97 vol. p. c.) ...... $c = 2$, $[\alpha]_D^{15} = -218.6°$ [1]
" (97 " ") ...... $c = 2$, $[\alpha]_D^{25} = -215.5$
" (97 " ") ...... $c = 1$, $[\alpha]_D^{22.5} = -216.4$
Chloroform ...... $c = 5$, " $= -229.5$

Hydrochloride, $C_{19}H_{21}NO_3.HCl + H_2O$. Rhombic prisms

Water ...... $c = 2$ to 4, $[\alpha]_D^{15} = -168.32 + 2.33c$ [2]
" ...... $c = 2$, $[\alpha]_D^{22.5} = -163.25$
10 mol. HCl + water ...... $c = 2$, " $= -158.6°$

PSEUDOMORPHINE (Oxydimorphine, Dehydromorphine)

Hydrochloride, $C_{34}H_{36}N_2O_6.HCl + H_2O$.[3]

1 mol. HCl + water ...... $c = 0.8$ to 1.6, $[\alpha]_D^{22.5} = -114.76 + 4.96c$ [4]
5½ mol. Na_2O + water ...... $c = 2$, " $= -198.9°$

$C_{17}H_{17}NO_3.HCl$ (at 100°)
$p = 0.951$, $d_D^{24} = 1.0044$, $[\alpha]_D^{24} = -103.13°$ [5]

LAUDANINE, $C_{20}H_{24}NO_4$. Rhombic crystals, melting-point, 166°.

Chloroform ...... $c = 2$, $[\alpha]_D^{22.5} = -13.5°$ [6]
2 mol. Na_2O + water ...... $c = 1$, " $= -11.4$
Chloroform ...... $p = 3.035$, $[\alpha]_D^{21} = +0.057°$

This number lies within the limits of experimental error, and Goldschmidt,[7] therefore, considers laudanine inactive.

Hydrochloride, $C_{20}H_{25}NO_4.HCl + 6H_2O$. Inactive [8]

LAUDANIDINE, $C_{17}H_{15}N(OH)(OCH_3)_3$. Melting-point, 177°
$[\alpha]_D = -87.8°$ [9]

LAUDANOSINE, $C_{21}H_{27}NO_4$. Crystals; melting-point, 89°

Alcohol (97 vol. p. c.) ...... $c = 2.79$, $[\alpha]_D^{15} = +103.2°$ [10]
" (97 " ") ...... $c = 2$, $[\alpha]_D^{22.5} = +105.0$
Chloroform ...... $c = 2$, " $= +56.0$
2 mol. HCl + water ...... $c = 2$, " $= +108.4$

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[1] Hesse. Ann. Chem. (Liebig), **176**, 196.
[2] Hesse. *Loc. cit.*, p. 197.
[3] Hesse. Ann. Chem. (Liebig), **235**, 229.
[4] Hesse. *Ibid.*, **176**, 195.
[5] Donath. J. prakt. Chem., [2], **33**, 562.
[6] Hesse. Ann. Chem. (Liebig), **176**, 201.
[7] Wiener Monatsh. Chem., **13**, 693.
[8] Hesse. *Loc. cit.*
[9] Hesse. Ann. Chem. (Liebig), **282**, 208.
[10] Hesse. *Ibid.*, **176**, 202.

Papaverine, $C_{20}H_{21}NO_4$. Triclinic prisms; melting-point 147°. The earlier figures of Hesse[1]

Alcohol (97 vol. p. c.)............... $c = 2$, $[\alpha]_D^{15} = -4.0°$
Chloroform....................... $c = 2$, " $= -5.7$

are wrong, according to Goldschmidt;[2] the papaverine formula contains no asymmetric carbon atoms, in consequence of which the alkaloid must be inactive, as Hesse gives for the hydrochloride. Goldschmidt found:

Chloroform ...... $c = 17.8$, $[\alpha]_D^{15} = +0.11°$

Tetrahydropapaverine, $C_{20}H_{25}NO_4$. The dextro and levo bases have been obtained by Pope and Peachey[3] by resolution of the racemic compound by dextro-α-bromocamphorsulphonic acid.

l-Base......... $c = 4.0032$, $[\alpha]_D = -143.4°$
d-Base......... $c = 4.3376$, $[\alpha] = +153.7$

Because of difficulties in the purification of the separated bases, the rotations are probably not quite accurate.

Cryptopine, $C_{21}H_{23}NO_5$. Crystals; melting-point, 217°. The alkaloid is inactive, dissolved in chloroform or hydrochloric acid.[4]

Narcotine (Opianine), $C_{22}H_{23}NO_7$. Crystals; melting-point, 176°

Alcohol (97 vol. p. c.)................. $c = 0.74$, $[\alpha]_D^{22.5} = -185.0°$
Chloroform mixture........ ... ... $c = 2$, " $= -191.5$
Chloroform .... $c = 2$ to 5, " $= -207.35$
2 mol. HCl + water.. .. .. $c = 2$, " $= +47.0$
2 " " + " .. .. $c = 5$, " $= +46.4$
10 " " + " .... $c = 2$, " $= +50.0$
Alcohol (80 vol. p. c.) + 2 mol. HCl.. $c = 2$, " $= +115.5$ [5]
Benzene, $p = 1.59$, $[\alpha]_D = -229°$; dilute oxalic acid, $[\alpha]_D = +62°$[6]

Pseudonarceine, $C_{23}H_{27}NO_8 + 3H_2O$. Crystals; melting-point, about 175°. Is inactive in acetic acid solution.[7]

Narceine, inactive in neutral or acid solution.[8]

[1] Ann Chem (Liebig), **176**, 198
[2] Wiener Monatsh Chem, **13**, 691.
[3] J Chem Soc, **73**, 893
[4] Hesse Ann Chem (Liebig), **176**, 200.
[5] Hesse *Ibid*, **176**, 192.
[6] Dott Ber d chem Ges, **17**, Ref 77.
[7] Roser Ann Chem (Liebig), **247**, 169
[8] Hesse *Ibid*, **176**, 198

Strychnos Alkaloids

STRYCHNINE, $C_{21}H_{22}N_2O_2$. Rhombic columns; melting-point, 284°

Alcohol ($d = 0.865$) . . $c = 0.91$, $[\alpha]_D = -128°$ [1]
Chloroform . . . . $c = 4$, " $= -130$
" . . . . $c = 2.25$, " $= -137.7$
" . . . . $c = 1.5$, " $= -140.7$
Amyl alcohol . . . . $c = 0.53$ " $= -235$
Alcohol ($d = 0.8543$) . . . $c = 0.25$, $[\alpha]^{20}_D = -114.7°$ [2]
" ($d = 0.8543$) . . . $c = 0.10$, " $= -119.3$

Other constants are given by Wyrouboff[3] on strychnine, strychnine sulphate, and selenate, but without statement as to *l*, *c* or *t*.

The effect of acids (HCl, $HCHO_2$, $HC_2H_3O_2$, H_2SO_4, H_2CrO_4, H_3PO_4, H_3AsO_4, $H_3C_6H_5O_7$) on the specific rotation of strychnine was investigated by Tykociner[4]

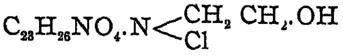
Desoxystrychnine Hydrochloride, $C_{21}H_{26}N_2O\ HCl$ (at 100°). Crystals.

Water . . . . $c = 10$, $[\alpha]_D = -16.0°$ [5]

BRUCINE, $C_{23}H_{26}N_2O_4 + 4H_2O$ Monoclinic crystals, melting-point, 178°.

Alcohol ($d = 0.865$) . . . . . $c = 5.4$, (anhydrous), $[\alpha]_D = -85°$ [6]
Chloroform . . . . $c = 1.9$, " " $= -127$
" . . . . $c = 4.9$, " " $= -119$
Absolute alcohol . . . . $c = 2.129$, " $[\alpha]^{20}_D = -80.1°$ [7]

Effect of acids, see under strychnine[8]

Oxyethylbrucine Chloride, 

$C_{23}H_{26}NO_4.N{<}^{CH_2\ CH_2.OH}_{Cl}$

Colorless, columnar crystals, melting-point, 185°.

Water . . . . $c = 4.5$, $[\alpha]^{20}_D = -4.50°$ [9]

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[1] Oudemans Ann Chem (Liebig), **166**, 76
[2] Tykociner Rec trav chim Pays-Bas, **1**, 146
[3] Compt rend, **115**, 832
[4] *Loc cit*
[5] Tafel Ann Chem (Liebig), **268**, 245
[6] Oudemans *Ibid*, **166**, 69
[7] Tykociner Rec trav chim Pays-Bas, **1**, 148
[8] Tykociner *Loc cit*
[9] Meulenhoff: Centrbl, 1893, II, 761

Other Alkaloids, and Bases

CORYDALINE, $C_{22}H_{27}NO_4$. From *Corydalis cava*. Crystals; melting-point, 134°.

Chloroform..... $c = 6\ 55$, $[\alpha]_D^{16} = +\ 300\ 1°$[1]

BULBOCAPNINE, $C_{19}H_{19}NO_4$ From *Corydalis cava*. Monoclinic columns; melting-point, 199°.

Chloroform..... $c = 4\ 48$, $[\alpha]_D^{16} = +\ 237\ 1°$[2]

CYTISINE (Ulexine, Sophorine), $C_{11}H_{14}N_2O$. Colorless crystals; melting-point, 150° to 151.5° (uncorr.)

Water .... $c = 2$, $[\alpha]_D^{12} = -\ 120°$
Alcohol (90 vol p c.). . $c = 2$, " $= -\ 100.42$
Chloroform ... . $c = 2$, " $= -\ 65\ 42$ [3]

Nitrate, $C_{11}H_{16}N_2O.NO_3H + H_2O$. Crystals.

Water........ ... $c = 5$, $[\alpha]_D^{11} = -\ 90\ 17°$
" .... $c = 2.5$ " $= -\ 89.33$ [4]

DELPHININE, $C_{22}H_{35}NO_6$ (at 100°). Rhombic crystals.

DELPHINOIDINE, $C_{42}H_{68}N_2O_7$. Crystals; melting-point, 110° to 120°

STAPHISAGRINE, $C_{22}H_{33}NO_5$. Amorphous.

The last three alkaloids are inactive in alcoholic solution.[5]

ECHITAMINE, $C_{22}H_{28}N_2O_4 + 4H_2O$ Crystals.

Alcohol (97 vol p c)...... ... $c = 2$, $[\alpha]_D^{15} = -\ 288°$

According to Hesse,[6] it is identical with Harnack's ditaine.[7]

IMPERIALINE, $C_{35}H_{60}NO_4$(?) Needles; melting-point, 254°.

Chloroform . . . . $p = 5.262$, $[\alpha]_D = -\ 35\ 40$[8]

PILOCARPINE, $C_{23}H_{34}N_4O_4 + 4H_2O$. Tough colorless mass.
(Solvent?) $c = 7\ 24$, $[\alpha]_D = +\ 101\ 6°$, $c = 25.89$, $[\alpha]_D = +\ 87\ 77°$[9]

A review of recent determinations on pilocarpine is given by Jowett,[10] and the optical rotation of the base and salts has been measured. The formula of the base is taken as $C_{11}H_{16}O_2N_2$

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[1] Freund, Joseph Ann Chem (Liebig), **277**, 7
[2] Freund, Joseph *Ibid*, **277**, 12
[3] van de Moer Arch d Pharm, **229**, 57
[4] van de Moer *Loc. cit*
[5] Marquis Jahresbericht, 1877, p 896
[6] Ann Chem (Liebig), **203**, 144
[7] Ber d chem. Ges, **11**, 2004
[8] Fragner *Ibid*, **21**, 3284
[9] Poehl Jahresbericht, 1880, p 993, 1075
[10] J Chem Soc, **77**, 473

Base, chloroform? $c = 1$ to 20, $[\alpha]_D = + 100.5°$

For the salts, the solvent used appears to be alcohol or water.

Nitrate, $C_{11}H_{16}O_2N_2.HNO_3$,	$c = 9.572$,	$[\alpha]_D = + 82.90°$
Hydrochloride,	$c = 9\ 924$,	" $= + 91\ 74°$
Hydrobromide,	$c = 10.058$,	" $= + 77.05°$
Sulphate,	$c = 7.318$,	" $= + 84\ 72°$

ISOPILOCARPINE, $C_{11}H_{16}N_2O_2$.

Base ………………	$c = 11\ 652$,	$[\alpha]_D = + 42.91°$	[1]
Nitrate ……………	$c = 6.586$,	" $= + 35\ 68$	
Hydrochloride ………	$c = 4.974$,	$[\alpha] = + 38.8$	
Hydrobromide ………	$c = 2\ 288$,	" $= + 32\ 8$	

PILOCARPIDINE, $C_{10}H_{14}O_2N_2$.

Base ………………	$c = 1.5374$,	$[\alpha]_D = + 81\ 3°$	[2]
Nitrate ……………	$c = 7.104$,	" $= + 73\ 2$	

PIPERINE. Inactive.

SPARTEINE $C_{15}H_{26}N_2$. Thick oil, colorless and odorless. Boiling-point, 180° to 181° (20 mm.).

Alcohol (96 p c) ………… $c = 23\ 88$, $[\alpha]_D^{26} = - 14\ 6°$ [3]

d-α-PIPECOLINE (α-Methylpiperidine), $C_5H_{10}N.CH_3$. By resolution of the racemic synthetic α-pipecoline by means of *d*-tartaric acid. Boiling-point, 118° to 119° [4]

$d^0 = 0.860$, $[\alpha]_D = + 21\ 73°$ [5]

Purest preparation · $[\alpha]_D = + 37.29, 36\ 9, 37\ 2°$ [6]

d-CONINE (*d*-α-*N*-Propylpiperidine), $C_5H_{10}N.C_3H_7$.

1. Natural Conine From *Conium maculatum.*

$d^{15} = 0.873$, $[\alpha]_D = + 15\ 6°$ [7]

$d^{20} = 0\ 845$, $[\alpha]_D = + 13\ 79$ [8]

$d = 0.845$, b p 166° to 167°, $[\alpha]_D = + 15\ 6°$ [9]

$d^{19} = 0.8438$, b p 165 7 to 165 9 (759 mm.), $[\alpha]_D^{19} = + 15.7°$ [10]

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[1] Jowett *Loc cit* Solvent not given

[2] Jowett *Loc. cit* Solvent not clearly given.

[3] Bernheimer Gazz chim ital, **13**, 451

[4] Ladenburg Ann Chem (Liebig), **247**, 65

[5] Ladenburg *Loc cit* (1888)

[6] Ladenburg, Ber. d. chem Ges, **27**, 856, 3063 (1894)

[7] H Schiff Ann Chem (Liebig), **166**, 94 (1873)

[8] Ladenburg *Ibid*, **247**, 86 (1888)

[9] Ladenburg. Ber. d. chem Ges, **27**, 858 (1894)

[10] Wolffenstein *Ibid.*, **27**, 2612

2. *Artificial Conine*, by resolution of *α-N*-propylpiperidine by means of *d*-tartaric acid.[1]

$$d^{20} = 0.845, \quad [\alpha]_D = +13.87°\,^{2}$$
$$d^{23} = 0.8438, \quad \text{b. p. } 167.7°, \quad [\alpha]_D = +18.3°\,^{3}$$

The following data on the specific rotation of conine and its salts are given by Zecchini.[4]

Name	Solvent	c.	t	$[\alpha]_D$
Conine	Benzene	13.094	24.2°	+ 9.54°
"	"	20.464	22.1	+ 9.77
"	"	33.290	23.9	+ 11.14
"	Alcohol	10.841	24.4	+ 8.12
"	"	15.172	22.7	+ 8.70
"	"	44.687	26	+ 9.98
"	Water	1.071	25.7	+ 1.21
Acetate	Benzene	22.854	25.7	+ 3.63
"	Alcohol	21.904	25.0	+ 2.35
"	Water	31.944	26.6	+ 1.16
Hydrochloride	Alcohol	6.722	25	+ 4.56
"	Water	11.458	26	+ 0.27
Hydrobromide	Alcohol	6.053	23.4	+ 4.28
"	Water	11.890	25.6	+ 0.27

Acetylconine, $C_8H_{16}N(C_2H_3O)$. Liquid; boiling-point, 125° (14 mm.)

$$d_{16} = 0.9616, \quad [\alpha]_D^{16} = +34.2°\,^{5}$$

Benzoylconine, $C_8H_{16}N(COC_6H_5)$, Liquid.

$$d_{16} = 1.0623, \quad [\alpha]_D^{16} = +29.1°\,^{6}$$

l-Conine Liquid.

Absolute alcohol .. . $c = 50$, $[\alpha]_D^{20} = +15.2°$[7]

N-Methylconine, $C_8H_{16}(CH_3)N$ Boiling-point, 173° to 174° (757 mm.).

$$d^{24.3} = 0.8318, \quad t = 24°, \quad [\alpha]_D = +81.33°\,^{8}$$

ISOCONINE (?), $C_8H_{17}N$.

$$[\alpha]_D = +8.19°\,^{9}$$

[1] Ladenburg See § 33, p 112

[2] Ladenburg Ann Chem (Liebig), **247**, 86 (1888).

[3] Ladenburg Ber d. chem Ges, **27**, 3066 (1894).

[4] Esperienze sul potere rotatorio della conina e dei suoi sali Roma, 1893.

[5] Ladenburg Ber. d. chem Ges, **26**, 854

[6] Ladenburg *Loc cit*

[7] Ladenburg Ann Chem (Liebig), **247**, 86

[8] Wolffenstein Ber d chem Ges, **27**, 2611

[9] Ladenburg *Ibid*, **26**, 854.

According to Wolffenstein,[1] this is a mixture of *d*-conine with inactive conine.

Benzoylisoconine, $C_8H_{16}N(COC_6H_5)$. Liquid.

$$d_{16} = 1.0623, \quad [\alpha]_D = + 29.1°\ ^{2}$$

β-PROPYL PIPERIDINE, $C_5H_{10}N\ C_3H_7$. The synthetic base has been resolved by means of tartaric acid by J. D. Granger.[3]

$$\textit{d-Base},\ d = 0.8517, \quad [\alpha]_D^{16} = + 6.39°$$
$$\textit{l-Base},\ d = 0.8517, \quad \text{''} \ = - 6.39°$$

α-ISOBUTYLPIPERIDINE (Homoconine), $C_5H_{10}N\ CH_2.CH(CH_3)_2$ Liquid ; boiling-point, 181° to 182° ; $d_4^0 = 0.8583$ Inactive[4]

Homoconic Acid, $C_{18}H_{17}NO_2$, and *Amido Valeric Acid*, $C_5H_{11}NO_2$, formed by the oxidation of conine, are inactive in 5 per cent. solution[5]

PARACONINE, $C_8H_{15}N$. Liquid , boiling-point, 168° to 170°. Inactive[6]

δ-CONICEINE, $C_8H_{15}N$. Liquid ; boiling-point, 168°

$$d_4^{23} = 0.8976, \quad [\alpha]_D = - 7.8°\ ^{7}$$

ε-CONICEINE, $C_8H_{15}N$. Liquid ; boiling-point, 150° to 151°.

$$[\alpha]_D = \text{about} + 42°\ ^{8}$$

The statement of Hesekiel[9] that β-picoline is active is an error, according to Landolt.[10]

NICOTINE, $C_{10}H_{14}N_2$. Boiling-point, 246.7 (745 mm.). $d_4^{20} = 1.01101$

$$[\alpha]^{20} = - 161.55°\ ^{11}$$
$$\text{''} \ = - 164.0\ ^{12}$$
$$[\alpha]_D^{18} = - 161.09\ ^{13}$$
$$[\alpha]_D^{20} = - 162.84, \quad d_4^{20} = 1.0107\ ^{14}$$

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[1] Ber d chem Ges., **29**, 1956
[2] Ladenburg *Loc cit*
[3] Ber d chem Ges , **30**, 1060
[4] Jacobi, Stoehr *Ibid* , **26**, 949
[5] Schotten *Ibid* , **19**, 503, 507.
[6] Michael *Ibid* , **14**, 2105
[7] Lellmann Ann Chem (Liebig), **259**, 199.
[8] Lellmann, p 203
[9] Ber d chem Ges , **18**, 3091
[10] *Ibid* , **19**, 157
[11] Landolt, § 52 Ann Chem (Liebig), **189** 241
[12] Hein Inaug Diss , Berlin, 1896
[13] Nasini and Pezzolato Ztschr phys Chem , **12**, 501
[14] Gennari *Ibid* , **19**, 130, § 46

Rotation dispersion of nicotine.[1]
Effect of temperature between 10° and 30°.[2]
Solutions in water.[3]
Solutions in water, great dilution.[4]
Solutions in water, increase of rotation on standing.[5]
Solutions in ethyl alcohol.[6]
Solutions in propyl alcohol, ether, acetone.[7]
Solutions in benzene.[8]

NICOTINE SALTS. Right-rotating.

Hydrochloride, $C_{10}H_{14}N_2.HCl$.

Water, $[\alpha]_D^{20} = +51.50 - 0.7931\,q + 0.004238\,q^2$, for $q = 57$ to 90, from which for

$$p = 10\quad [\alpha]_D^{20} = +14.44;\quad p = 30:\ [\alpha]_D^{20} = +16.75^\circ$$ [9]

Neutral Sulphate, $(C_{10}H_{14}N_2)_2.H_2SO_4$.

Water, $[\alpha]_D^{20} = +19.77 - 0.05911\,q$, for $q = 30$ to 90, from which for

$$p = 10\quad [\alpha]_D^{20} = +14.52,\quad p = 30\quad [\alpha]_D^{20} = +15.64^\circ$$ [10]

Acetate, $C_{10}H_{14}N_2.C_2H_4O_2$.

Water, $[\alpha]_D^{20} = +49.680 - 0.6189\,q + 0.002542\,q^2$, for $q = 77$ to 95, from which for

$$p = 10.\ [\alpha]_D^{20} = +14.57^\circ;\ p = 30\cdot\ [\alpha]_D^{20} = +18.81^\circ$$ [10]

Water.... $[\alpha]_D^{20} = +13.204 + 0.11406\,c + 0.002073\,c^2$, to $c = 65$ [11]

On the behavior of a left-rotating equimolecular mixture of nicotine and glacial acetic acid on dilution with water, see §46, p. 161. For solutions of nicotine acetate in alcohol:

$$c = 12.97:\ [\alpha]_D^{20} = -65.27^\circ,\ c = 51.12\cdot\ [\alpha]_D^{20} = -58.94^\circ$$

On addition of water to the alcoholic nicotine acetate solution, the rotation becomes right-handed; conversely, aqueous solutions of the salt become left-rotating on addition of alcohol. The aqueous solutions of the sulphate and hydrochloride, which are right-rotating, behave in the same manner

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[1] Gennari, § 46, p. 160
[2] Landolt, § 60, p. 208.
[3] Landolt, § 52, p. 181
[4] Pribram, Hein, § 56, p. 198
[5] Pribram, § 76, p. 282
[6] Landolt, § 52, p. 182, Hein, § 62, p. 229.
[7] Hein, § 62, p. 229; Nasini and Gennari: Ztschr. phys. Chem., 19, 117, § 46, p. 163.
[8] Hein, § 48
[9] Schwebel: Ber. d. chem. Ges., 15, 2850.
[10] Schwebel
[11] Nasini and Pezzolato: Ztschr. phys. Chem., 12, 501

The separation of nicotine from the alcoholic solutions of its salts, by means of triethyl amine, aniline, and ammonia, may be followed by the polariscope, a method of determining nicotine is based on the complete displacement by solutions of potassium and sodium hydroxides. The decompositions are not absolutely complete in aqueous solutions [1]

Boric acid added to an alcoholic solution of pure nicotine produces a slight decrease in the left rotation.

HYDRONICOTINE, $C_{10}H_{16}N_2$. Boiling-point, 263° to 264°. $d^{17} = 0\ 993$.

Water .... $c - 13.7°$, $[\alpha]_D = -15.40$ [2]

d-COPELLIDINE, $C_8H_{17}N$. Boiling-point, 162° to 163°. $d = 0\ 838$.

$d = 0.8381$, $[\alpha]_D = +36\ 50°$ [3]
$d^{15} = 0.8375$, " $= +36\ 93$ [4]

l-COPELLIDINE. Boiling-point, 162° to 164°.

$d = 0.8386$, $[\alpha]_D = -\ 7.91°$ [3]
$d^{19} = 0.8347$, " $= -16.26°$ [4]

d-ISOCOPELLIDINE, $C_8H_{17}N$. Boiling-point, 103° to 166°.

$d^{18} = 0\ 8500$, $[\alpha]_D = -25\ 93°$ [4]

l-ISOCOPELLIDINE Boiling-point, 162.2° to 162.5°

$d = 0\ 8445$, $[\alpha]_D = -25\ 93°$ [3]
$d^{17} = 0\ 8435$, " $= -57\ 03$ [4]

TETRAHYDROQUINALDINE, $C_{10}H_{13}N$. The racemic base has been split by Pope and Peachey[5] by the dextrocamphorsulphonic acid method. They give for the

l-Base, $d_4^{14\ 5} = 1.02365$, $[\alpha]_D^{20} = -58.12°$
d-Base, $d_4^{20} = 1\ 0192$, $[\alpha]_D^{20} = +58\ 09$

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[1] Pezzolato Gazz chim ital, 10, 780

[2] Etard Compt rend, 97, 1219

[3] Levy, Wolffenstein Ber d chem Ges, 28, 2271.

[4] Levy, Wolffenstein *Ibid*, Ges, 29, 1960

[5] J Chem Soc, 75, 1066

For the *d*-base, Ladenburg[1] found nearly the same value after tartaric acid resolution. In their paper, Pope and Peachey give the constants for salts and other derivatives.

27. Glucosides

SALICIN, $C_{13}H_{18}O_7$.

Water.......... p 1 to 3, $[\alpha]_D^{15}$ = 65.17 + 0.63p [2]

Water.......... p 4.938, d_4^{20} = 1.0135, $[\alpha]_D^{20}$ = − 62.56 [3]

Water.......... p 2.78, $[\alpha]_D$ = 73.4° [4]

Alcohol (50 p. c.), $[\alpha]_D$ 50.30 − 0.05026q,

t 22° to 26°, q = 90 to 96 [5]

HELICIN, $C_{13}H_{16}O_7 + {}^3/_4H_2O$.

Alcohol (50 p. c.)...... t = 20°, p = 3 to 9, $[\alpha]_D$ = − 47.03° [6]

Water...... p 1.351 (anhydrous), d_4^{20} = 1.0084, $[\alpha]_D^{20}$ = − 60.43° [9]

POPULIN, $C_{20}H_{22}O_8$.

Water.............. p 1, $[\alpha]_D$ = − 53° [7]

PHLORIDZIN, $C_{21}H_{30}O_{11} + 2H_2O$.

Alcohol (97 p. c.).... p 1 to 5, $[\alpha]_D^{22.5}$ = − 49.40 − 2.41p [8]

Alcohol.............. p 4.6, $[\alpha]_D$ = − 52° } [9]

Wood alcohol ...... p 3.9, " − 52 }

AMYGDALIN, $C_{20}H_{27}NO_{11} + 3H_2O$.

$[\alpha]_D$ = − 35.5° [10]

APIIN, $C_{27}H_{32}O_{16}$. Weak alcoholic solution

$[\alpha]_D$ = + 173° [11]

CONIFERIN, $C_{16}H_{22}O_8 + 2H_2O$

Water...... p 0.621 (anhydrous), d_4^{20} 0.9998, $[\alpha]_D^{20}$ = − 66.90° [9]

GLUCOVANILLIN, $C_{14}H_{18}O_8 + 2H_2O$

Water........ p 0.896 (anhydrous), d_4^{20} 1.0011, $[\alpha]_D^{20}$ 88.63° [9]

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[1] Ber. d. chem. Ges., **27**, 75

[2] Hesse. Ann. Chem (Liebig), **176**, 116

[3] Wegscheider: Ber. d. chem. Ges, **18**, 1600

[4] Biot, Pasteur: Compt. rend, **34**, 607

[5] Sorokin: J prakt Chem., [2], **37**, 320

[6] Sorokin. *Ibid.*, [2], **37**, 291.

[7] Biot, Pasteur. *Loc. cit.*

[8] Hesse: Ann Chem (Liebig), **176**, 117.

[9] Oudemans. *Ibid.*, **166**, 69.

[10] Bouchardat: Compt rend., **19**, 1174.

[11] Lindenborn, Gerichten: Ber. d. chem Ges., **9**, 1123.

CONVALLAMARIN, $C_{23}H_{44}O_{12}$.

Alcohol .... $[\alpha]_D = -55°$[1]

DIGITONIN, $C_{27}H_{46}O_{14} + 5H_2O$.

Acetic acid (75 p c) · $p = 2\ 8$, $[\alpha]_D = -50°$[2]

IVY LEAF GLUCOSIDE, $C_{32}H_{54}O_{11}$

Alcohol .... $t = 22°$, $[\alpha]_D = -47\ 5°$[3]

ISOHESPERIDIN, $C_{22}H_{26}O_{12} + 2H_2O$

Alcohol .... $[\alpha]_D = -89°$[4]

NARINGIN (Aurantiin, Hesperidin), $C_{21}H_{26}O_{11}$.

Water .... $c = 20.46$, $t = 17°$, $[\alpha]_D = -84.5°$[5]
Alcohol ... $c = 7\ 299$, $t = 17$, $[\alpha]_D = -87\ 6$

OUBAIN, $C_{30}H_{46}O_{12} + 7H_2O$.

Water .... $p = 0\ 65$, $[\alpha]_D^{10} = -34°$[6]

PICEIN, $C_{14}H_{18}O_7 + H_2O$.

Water .... · $p = 2.5$, $[\alpha]_D = -84°$[7]

CONVOLVULIN, $C_{61}H_{108}O_{27}$ Melting-point, 140° to 148°.

Alcohol .... $[\alpha]_D = -36\ 9°$[8]

In addition, E. Fischer has produced a series of simple glucosides synthetically and has determined their constants of rotation

	Solvent	p	$d\,^{20}_{20}$	$[\alpha]^{20}_{D}$.	E. Fischer
α-Methyl-*d*-glucoside	Water	5	.	+ 157 6°	28, 115
α- " -*l*- "	"	5		— 156 9	28, 115
α-Ethyl-*d*- "	"	9 002	1.025	+ 150 6	28, 1154
	"	8 897	..	+ 150 3	28, 1154
α-Methyl galactoside	"	9.119	1 026	+ 179 0	28, 1155
β- " "[10]	Borax sol	8.5	.	+ 2 6	28, 1155
Ethyl "	Water	9.47	1.0273	+ 178 75	27, 2481
Benzyl arabinoside	"	1 03	1 0013	+ 215.2	27, 2482
Methyl glucoheptoside	"	10 06	1 0338	— 74.7	28, 1156
α-Methyl xyloside	"	9 32	1 026	+ 153 2	28, 1158
β- " "	"	9 14	1.024	— 65 9	28, 1157
Methylrhamnoside ..	"	9.68	1 024	— 62 2	28, 1159
" sorboside	"	9.12	1 028	— 88.5	28, 1160
	"	8 19	1.026	— 88 9	28, 1160
Mandelnitrile glucoside ..	"	8 25	1 018	— 26.9	28, 1509
Acetone rhamnoside .	"	9.16	1 017	+ 17.4	28, 1163
Diacetone arabinoside	"	2 41	1 003	+ 5 4	28, 1164
" glucoside	"	4 93	1 008	— 18 5	28, 1167
" fructoside	"	7 29	1 014	— 161 3	28, 1165
Triacetone mannitol .	Alcohol	9 58	0 811	+ 12.5	28, 1168

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[1] Tanret Jahresbericht, 1882, p 1130

[2] Kiliani Ber d chem Ges., **24**, 339

[3] Vernet Jahresbericht, 1881, p 991

[4] Tanret Bull soc chim, [2], **49**, 21.

[5] Will · Ber d chem Ges, **20**, 294

[6] Arnaud Compt rend., **107**, 1162

[7] Tanret Bull soc chim, [3], **11**, 944

[8] Kromer Chem Centrbl., (1894), I, 635

[9] Ber d chem Ges

[10] In aqueous solution inactive

Also: *d*-and *l*-Methylmannoside.

	Water.......	p 8,	$[\alpha]_D$	± 70.2 to 79.4°[1]
d-form	Water.......	p 1,	"	+ 82.5° [2]
	"	p 8,	"	+ 79.2 [2]
	Alcohol	p 1,	"	= + 87.3 [2]

28. Bitter Principles and Indifferent Bodies

Santonin Group

The following data, unless otherwise stated, are from Carnelutti and Nasini.[5] According to these authors the concentration is without effect on the rotation:

Substance	Solvent. Per cent	t	c	$[\alpha]_D$	Observer
Santonin	Alcohol 97	15°	2	− 174.0°	Hesse[4]
"	" 90	15	2	− 175.4	
"	" 80	15	2	− 176.5	
"	Chloroform	15	2–10	− 171.5	
"	"	26	6	171.37	
Metasantonin	"	26	1.5	+ 292.15	
Santonide	"	26.5	1.5	+ 744.61	
"	"	20	3.1–30.5	+ 754	Nasini[6]
Metasantonide	"	26	1.5	− 223.46	
Parasantonide	"	26	1.5	+ 897.25	
"	"	20	2.6–50	+ 891.7	Nasini[6]
Santonic acid	"	26.5	6	− 70.31	
Methyl ester........	"	26.5	6	52.33	
Ethyl ester	"	26.5	6	45.35	
n-Propyl ester	"	26.5	6	39.31	
Allyl ester.........	"	26.5	6	39.54	
i-Butyl ester.......	"	27	6	− 41.63	
Parasantonic acid	"	26	6	− 98.51	
Methyl ester......	"	26	6	108.91	
Ethyl ester.......	"	26	6	− 99.98	
Propyl ester	"	26	6	91.27	
Santonyl chloride	"	26.5	6	− 13.14	
Santonyl bromide	"	26	6	− 100.53	
Santonyl iodide.......	"	26	6	99.21	

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[1] Fischer, Beensch: Ber. d. chem. Ges., **29**, 2927.

[2] Ekenstein. Rec. trav. chim. Pays-Bas, **15**, 221.

[3] Ber. d. chem. Ges., **13**, 2208.

[4] Ann. Chem. (Liebig), **176**, 125.

[5] R. Accad. Lincei, **13**, 1892.

[6] *Loc. cit.*

Substance	Solvent Per cent	t	c	$[\alpha]_D$	Observer
Photosantonin	Alcohol	14	2	— 121.6	Villavecchia[1]
Isophotosantonin	"	13	0 7	+ 76.77	
Dehydrophotosantonic acid	"	20	1.4	+ 31 9	
Diethyl ester.......	"	20	2 8	+ 20.4	
Isophotosantonic acid ...	"	11	2.4	+ 124.17	Cannizzaro, Fabris.[2]
Monoacetylisophotosantonic acid.	"	17	0 9	+ 58 6	
Santoninic acid	" 97%	22.5	1–3	— 25.8	Hesse[3]
" "	" 80%	22.5	2–3	— 26.5	
Na salt	Water	22 5	2	— 19 36	
Hyposantoninic acid.. .	...	..	....	— 4.62	Gucci and Grassi-Cristaldi[4]
Dihydrosantinic acid....	. ..	.	...	+ 62.07	
Santinic acid	....	..	....	+ 64 37	
Santoninaminesulphate..	..	.	....	— 103.67	
Santoninamine hydrochloride	. ..	..	.	— 136 83	

The following data are given by Nasini[5] for the specific rotation of some bodies of the santonin group for light of different colors

Spectrum line	Wave-length	Santonin		Meta-santonin. Chloroform $c = 2\ 206$ $t = 20^\circ$	Santonide		Para-santonide Chlorof $c = 3$ to 50 $t = 20^\circ$	Santo aci Chlor $c = 27$ $t = 2$
		Chloroform $q = 75$ to $96\ 5$ $t = 20^\circ$	Alcohol $c = 1\ 782$ $t = 20^\circ$		Alcohol $c = 4\ 046$ $t = 20^\circ$	Chlorof $c = 3$ to 30 $t = 20^\circ$		
B	686 7	— 140 1 + 0.2085 *q*	— 110 4	+ 92	+ 442	+ 484	+ 580.5	—
C	656 2	— 149 3 + 0 1555 *q*	— 118.8	+ 104	+ 504	+ 549	+ 655 6	—
D	589 2	— 202 7 + 0 3086 *q*	— 161.0	+ 124	+ 693	+ 754	+ 891 7	—
E	526 9	— 285 6 + 0.5820 *q*	— 222 6	+ 167	+ 991	+ 1088	+ 1264	— 1
b_1	518 3	— 302.38 + 0 6557 *q*	— 237 1	+ 182	+ 1053	+ 1148	+ 1334	— 1
F	486 1	— 365 55 + 0 8284 *q*	— 261 7	+ 217	+ 1323	+ 1444	+ 1666	— 1
e	438 3	— 534.98 + 1 5240 *q*	— 380 0	+ 257	+ 2011	+ 2201	+ 2510	— 1
g	422.6	......	....	...	+ 2381	+ 2610	+ 2963	— 2

[1] Ber d chem Ges, **18**, 2859

[2] *Ibid*, **19**, 2260

[3] Ann Chem (Liebig), **176**, 125

[4] Gazz chim ital, **22**, 1

[5] R Accad Lincei, [3], **13**, 1882

Andreocci[1] gives:

d-Disantonious acid........ .... $[\alpha]_D = +85.9°$
l- " " .... " $= -85.8$
d-Santonious " .... " $= +74.6$
l- " " .... " $= -74.3$
Desmotropodisantonious acid.... " $= -64.5$
Desmotroposantonious acid...... " $= -53.3$

Other Vegetable Substances

ASEBOTOXIN (Andromedotoxin), $C_{31}H_{51}O_{10}$.
Water........... ...... $c = 2.8$, $[\alpha]_D^{12} = -9.7°$ [2]
Chloroform.. .... $c = 0.41$, " $= +10.1$

PICROTOXIN, $C_{12}H_{14}O_5$.
Alcohol.............. $p = 3.125$, $[\alpha]_j = -28.1°$ [3]

ECHICERIN, $C_{30}H_{48}O_2$.
Ether. .. .. $c = 2$, $[\alpha]_D^{15} = +63.75°$ [4]
Chloroform ... . $c = 2$, " $= +65.75$

ECHITIN, $C_{32}H_{52}O_2$
Ether...... .... $c = 2$, $[\alpha]_D^{15} = +72.5°$ [5]
Chloroform .... $c = 2$, " $= +75.3$

ECHITEIN, $C_{42}H_{70}O$
Ether .... $c = 2$, $[\alpha]_D^{15} = +88°$ [5]
Chloroform .. .. $c = 2$, " $= +85.5$

ECHIRETIN, $C_{35}H_{56}O_2$
Ether..... . .... . $c = 2$, $[\alpha]_D^{15} = +54.8°$ [5]

EUPHORBON, $C_{15}H_{24}O$.
Ether......... ..... $c = 4$, $[\alpha]_D^{15} = +11.7°$ [6]
Chloroform .... $c = 4$, " $= +18.8$

ANTIARONIC ACID, $C_6H_{10}O_5$ (from *Antiaris toxicaria*).
Water..... .. .. $[\alpha]_D = +30°$ [7]

LUPEOL, $C_{26}H_{42}O$?.
Ether.... . ... $c = 9.97$, $[\alpha]_D = +27°$ [8]

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[1] Atti R Accad Lincei, [5], **4**, 164
[2] Zaayer Rec trav chim Pays-Bas, **5**, 313
[3] Bouchardat and Boudet J pharm chim, [3], **23**, 288
[4] Jobst and Hesse Ann Chem (Liebig), **178**, 49
[5] Jobst and Hesse *Loc cit*
[6] Hesse Ann Chem (Liebig), **192**, 195
[7] Kiliani. Arch. der Pharm, **234**, 438
[8] Likiernik Ztschr physiol Chem, **15**, 415

PHASOL, $C_{15}H_{24}O$
Chloroform .... $p = 4$, $[\alpha]_D = +30.6°$[1]

α-LACTACEROL, $C_{18}H_{30}O$.
Chloroform .... $p = 2.372$, $[\alpha]_D^{15} = +76.2°$

β-LACTACEROL, $C_{18}H_{30}O$
Chloroform .... $p \doteq 4$, $[\alpha]_D^{15} = +38.2°$[2]

QUEBRACHOL, $C_{20}H_{34}O$
Chloroform .... $p = 4$, $[\alpha]_D^{15} = -29.3°$[3]

CUPREOL, $C_{20}H_{34}O$.
Chloroform .... $p = 3.156$, $[\alpha]_D^{15} = -37.5°$[4]

CINCHOL, $C_{20}H_{34}O$.
Chloroform ... . $p = 6$, $[\alpha]_D^{15} = -34.6°$[5]

29. Biliary Substances

CHOLESTERIN, $C_{26}H_{44}O$(?) (melting-point, 145°) and $C_{26}H_{44}O + H_2O$.

Anhydrous ether. . .. . $c = 2$, $[\alpha]_D = -31.12°$[6]
" chloroform .. . $c =$ 2 5 8; $[\alpha]_D^{15} = -37.02$, -37.81, $-38.63°$
from which. $[\alpha]_D^{15} = -36.61 - 0.249\,c$

Solutions of the anhydrous substance in ether ($c = 7.941$), and in petroleum spirit ($c = 10$) gave, in agreement with each other, the following numbers.[7]

Light	*B*	*C*	*D*	*E*	b_2	*F*	*G*
$[\alpha] =$	-20.63	-25.54	-31.59	-39.91	-41.92	-48.65	-62.37

Cholesterin Ester of Oleic Acid, $C_{26}H_{43}O$ ($C_{18}H_{33}O$). From dog serum Melting-point, 41° to 45°.

Equal parts of alcohol + chloroform } $c = 7.94$, $[\alpha]_D = -18.80°$[8]

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[1] Likiernik Ztschr physiol Chem, **15**, 430
[2] Hesse Ann Chem (Liebig), **234**, 248
[3] Hesse *Ibid*, **211**, 272
[4] Hesse *Ibid*, **228**, 291
[5] Hesse *Ibid.*, **228**, 294
[6] Hesse *Ibid*, **192**, 178
[7] Lindenmeyer J prakt Chem, [1], **90**, 323
[8] Hürthle Ztschr physiol Chem, **21**, 337

PHYTOSTERIN, $C_{26}H_{44}O$ Melting-point, 132° to 133°.
Chloroform............ $p = 1.636$, $[\alpha]_D^{15} = -34.2°$[1]

PARAPHYTOSTERIN, $C_{24}H_{40}O$.
Chloroform............ $c = 3.45$, $[\alpha]_D = -44.1°$[2]

ISOCHOLESTERIN, $C_{26}H_{44}O$. Melting-point, 138° to 138.5°
Ether ... . $c = 7.344$, $[\alpha]_D = +60°$[3]
" ... . $c = 6.435$, " $= +59.1°$[4]

PARACHOLESTERIN, $C_{26}H_{44}O$. Melting-point, 134° to 134.5°
Chloroform .. . . $p = 2.7$, $d = 1.4717$, $[\alpha]_D^{20} = -28.88°$[5]

CAULOSTERIN, $C_{26}H_{44}O$ Melting-point, 158° to 159°.
Chloroform.......... . $c = 5.0905$, $[\alpha]_D = -49.6°$[6]

ERGOSTERIN, $C_{26}H_{40}O$
Chloroform.. .... $c = 3.33$, $[\alpha]_D = -114°$[7]

KOPROSTERIN, $C_{25}H_{44}O$ From human feces. Melting-point, 95° to 96°.
Ether.. .. $c = 13.2$ (1.581 gram subst. in 12 cc ether), $[\alpha]_D = +24°$[8]

GLYCOCHOLIC ACID, $C_{26}H_{43}NO_6$.
Alcohol .. . $c = 9.504$ Rotation independent of the concentration

Light	C	D	E	b_2	F	G
$[\alpha] =$	+ 21.6	+ 29.0	+ 37.9	+ 40.0	+ 48.7	+ 56.8[9]

Sodium Salt, $NaC_{26}H_{42}NO_6$
Alcohol .... $c = 20.143$, $[\alpha]_D = +25.7°$ }[9]
Water. .... $c = 24.928$, " $= +20.8$ }

The concentration is without influence

TAUROCHOLIC ACID, $C_{26}H_{45}NSO_7$.

Sodium Salt, $NaC_{26}H_{44}NSO_7$.
Alcohol.... . $c = 9.898$, $[\alpha]_D = +24.5°$, $[\alpha]_F = +39°$ }[10]
Water . .... $c = 8.856$, " $= +21.5$ " $= +34$ }

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[1] Hesse Ann Chem (Liebig), **192**, 177
[2] Likiernik Ztschr physiol Chem, **15**, 430
[3] Schulze Ber d chem Ges, **12**, 149
[4] Schulze, Barbieri J. prakt Chem [2], **25**, 170
[5] Reinke, Rodewald Ann Chem (Liebig), **207**, 229
[6] Schulze, Barbieri J prakt Chem, [2], **25**, 166.
[7] Tanret Ann. chim phys, [6], **20**, 289
[8] Bondzynski and Humnicki Ztschr physiol Chem, **22**, 396, Bondzynski Ber d. chem Ges., **29**, 476
[9] Hoppe-Seyler: J prakt Chem, [1], **89**, 261.
[10] Hoppe-Seyler *Loc cit.*, p. 263

The concentration is without influence.

CHOLALIC ACID, $C_{24}H_{40}O_5(+ H_2O)$ and $(+ 2^1/_2H_2O)$

a. Anhydrous Cholalic Acid.

From ox gall. Alcohol, $c = 3.338$, $[\alpha]_D = + 50\ 2°$ }[1]
" dog feces " $c = 2\ 942$, " $= + 47\ 6$ }

b Cholalic Acid with $2^1/_2$ mols. water of crystallization.[2]

	c Anhydrous	$[\alpha]_D$ Anhydrous	$[\alpha]_D$ Hydrated
Solutions in alcohol	6 070	+ 35 4°	+ 31 9°
	4 433	+ 34.8	+ 31 4
	2 707	+ 35.2	+ 31 7
	2 659	+ 33 9	+ 30.4
	2.030	+ 34 5	+ 31 1
	1.804	+ 34.2	+ 30 8

Cholalic acid with $2^1/_2$ mols water Alcohol, $c = 2.962$ (2 659 anhydrous) [3]

Line		*B*	*C*	*D*	*E*	b_2	*F*	*G*	
$[\alpha]$	For hydrated substance	+ 25.3	+ 27 0	+ 30.4	+ 40 1	+ 42.2	+ 47.3	+ 60 8	+
$[\alpha]$	For anhydrous substance	+ 28 2	− 30.1	+ 33.9	+ 44 7	+ 47 0	+ 52 7	+ 67 7	+

c. Cholalic Acid Alcoholate, $C_{24}H_{40}O_5 + C_2H_5OH$.[4]

Solution in alcohol of 97 volume per cent

p		d_4^t	*t*	*t*	$[\alpha]_D^{t'}$		*t''*
with crystal alcohol	pure acid				with crystal alcohol	pure acid	
1 9207	1 7262	0 81518	16.4	15	+ 31.30°	+ 34 83°	16 2
1 3340	1 1989	0.81050	23 4	23.4	+ 31.12	+ 34 63	23
1 1525	1 0358	0 81006	20.4	20.4	+ 31.30	+ 34 83	21
2 9204	2 6246	0 81493	21.1	21.1	+ 31.72	+ 35 29	21 2
0 9559	0 8591	0.81502	14 2	15	+ 32.02	+ 35.63	12 2
0 4794	0.4309	0 81260	13 4	15	+ 31.85	+ 35 44	14

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[1] Hoppe-Seyler *Loc. cit*, p 266

[2] Hoppe-Seyler. *Loc cit*, p 267

[3] Hoppe-Seyler J prakt. Chem, [1], 89, 267

[4] Vahlen Ztschr physiol. Chem, 21, 253

Potassium Salt, $KC_{24}H_{39}O_5$.

a. Aqueous solutions.

$c = 6.004$, $[\alpha]_D = +28.2°$ [1]
$c = 7.000$, " $= +27.5$
$c = 12.562$, " $= +25.9$
$c = 16.749$, " $= +24.6$
$c = 22.332$, " $= +24.1$
$c = 29.775$, " $= +24.9$

p	d.	t	$[\alpha]_D^t$
1.0433	1.0020	15	$+29.10°$ [2]
"	0.9993	30	$+30.79$
3.4940	1.00975	5	$+27.23$
"	1.00923	20	$+26.89$
5.4570	1.01498	11	$+27.69$
"	1.00695	40	$+27.06$
6.6825	1.01843	24	$+26.51$

b Alcoholic solutions

$p = 2.1178$, $d^{25} = 0.81027$, $[\alpha]_D^{25} = +31.60°$ [3]
p " $d^{17} = 0.81875$, $[\alpha]_D^{17} = +31.27$
$c = 4.22$

Light	C	D	E	b	F
$[\alpha] =$	$+23.7$	$+30.8$	$+38.5$	$+40.9$	$+47.5°$ [4]

Sodium Salt, $NaC_{24}H_{39}O_5$

a. Aqueous solutions.[5]

$c = 19.049$.

Light	B	C	D	E	b	F.
$[\alpha] =$	$+19.7$	$+21.0$	$+26.0$	$+33.1$	$+34.0$	$+42.0°$

---

[1] Hoppe-Seyler *J. prakt Chem.*, [1], 89, 270

[2] Vahlen: Ztschr physiol Chem, 21, 253.

[3] Vahlen.

[4] Hoppe-Seyler · *Loc cit.*, p. 269.

[5] Hoppe-Seyler *Loc cit*, p 271

p	d^t.	t	$[\alpha]^t_D$.
7.5888	1 01969	22 5°	+ 27 46° [1]
4 9450	1 01298	24	+ 28 19
4 0419	1 00826	20	+ 27 65
2 2920	1 00595	23	+ 30.61

From this, the specific rotation appears to be increased by lowering the concentration.

b. Alcoholic solution.

$c = 2\ 230$, $[\alpha]_D = + 31.4°$[2]

Cholalic Acid Methyl Ester, $CH_3.C_{24}H_{39}O_5$. Crystals

Alcohol .... $c = 4\ 59$, $[\alpha]_D = + 31.9°$

Cholalic Acid Ethyl Ester, $C_2H_5.C_{24}H_{39}O_5$. Crystals.[3]

Alcohol ... . $c = 18\ 479$

Light	B	D	E	b
$[\alpha] =$	+ 25.4	+ 32 4	+ 40 5	+ 42 3°

CHOLEINIC ACID, $C_{24}H_{40}O_4$(?). — $C_{25}H_{42}O_4$.[1]

Alcohol

p	d	t	$[\alpha]^t_D$.
2 469	0 8110	24°	+ 48.87°
1 786	0 8105	22	+ 49 52
0 862	0 8061	24	+ 48 60
0 694	0 8090	21	+ 52.49

CHOLANIC ACID. $C_{20}H_{30}O_7 + \frac{1}{4}H_2O$

Barium Salt, $Ba_3C_{20}H_{33}O$. $+ \frac{1}{4}H_2O$(?).

Water .... $p = 3\ 638$, $d = 1\ 017$, $[\alpha]_D = + 49\ 37°$[4]

DESOXYCHOLIC ACID, $C_{24}H_{40}O_4$

Alcohol, $p = 1\ 968$, $d^{23\ 4} = 0.81142$, $[\alpha]^{23\cdot4}_D = + 49\ 86°$[1]

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[1] Vahlen *Loc cit*

[2] Hoppe Seyler *Loc cit*, p 271

[3] Hoppe-Seyler *Loc cit* p 272

[4] Latschinoff Ber d chem Ges 19, 475

LITHOFELLINIC ACID, $C_{20}H_{36}O_4$. Melting-point, 205°.

Alcohol............ $[\alpha]_D = +13.76°$[1]

30. Gelatinous Substances

α-GLUTIN (ordinary glutin, gelatine).

Water, $c = 6.12$ $\begin{cases} t = 24 \text{ to } 25°, & [\alpha]_D = -130.0° \\ t = 35 \text{ to } 40, & \quad " \quad = -123.0 \end{cases}$

Water, $c = 3.06$ $\begin{cases} t = 24 \text{ to } 25, & \quad " \quad = -130.5 \\ t = 35, & \quad " \quad = -125.0 \end{cases}$

The rotation decreases, therefore, with the temperature; but, on the other hand, it does not appear to be much influenced by the concentration.

The effect of acids and alkalies is shown by the following experiments:

Glutin solution with $c = 3.06$:

Mixed with equal vol. of ammonia................ $[\alpha]_D = -130.5°$[2]
" " a few drops of sodium hydroxide...... " $= -130.5$
" " the same volume of hydroxide......... " $= -112.5$
" " " " " " acetic acid........ " $= -114.0$

The specific rotation of aqueous glutin solutions is decreased by long boiling.[3]

β-GLUTIN. Obtained by heating 1 part of gelatine with 2 to 3 parts of water, in a pressure bottle, for several days to 100°, until the liquid no longer solidifies on cooling.[4]

On account of lack of uniformity, the products showed differences in the rotating power.

Product with 1.40 p. c. ash. Water, $c = 5$, $[\alpha]_D^{15.5} = -130.6°$
" " 1.96 " " " $c = 5$, $[\alpha]_D^{17} = -125.8$

Multirotation was not detected.

The following observations were made on variations in the rotation.

1. The rotation of aqueous solutions decreases with increasing dilution.

$c =$	5	4	3	2	1
$[\alpha]_D^{16} =$	-120.7	-118.1	-117.5	-114.0	$-113.7°$

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[1] Roster. Gazz. chim. ital., 9, 364; Hoppe-Seyler and Thierfelder "Handb. d. phys. u. path.-chem. Analyse," 6 Aufl., p. 209.

[2] de Bary: Hoppe-Seyler's med.-chem. Untersuch., 1, 71.

[3] Nasse: Maly's Jahresbericht, 1889, p. 29.

[4] Framm: Arch. für die ges. Physiol., 68, 144 (1897).

2. The addition of methyl and ethyl alcohols in amount too small to produce precipitation, decreases the rotation.

3. Alkali chlorides (and also KI), and also alkali nitrates bring about a decrease in the rotation which is independent o time and temperature, but a chemical change in the glutin is not produced. Alkali sulphates have no similar action.

4. Acids diminish the rotation, and in greater degree the larger the amount used and the higher the temperature. The intensity of the action follows in the order: HCl, H_2SO_4, $HC_2H_3O_2$, H_3PO_4. The change does not increase with time. On neutralization of the acid the original value of the rotation is not restored.

5. Alkalies and ammonia (the last in concentrated condition only) diminish the rotation. The decrease becomes greater with time, and is not altered by neutralization of the alkali; a chemical change in the glutin is, therefore, produced.[1]

CHONDRIN. $c = 0.957$.

Water with a few drops of sodium hydroxide solution	$[\alpha]_j = -213.5°$	[2]
The liquid mixed with an equal volume of sodium hydroxide solution	" $= -552.0$	
The latter mixed with the same volume of water	" $= -281.0$	

31. Protein Bodies

SERUM ALBUMIN.

1	Neutral aqueous solution	$[\alpha]_D = -56°$	[3]
	Aqueous solution, saturated with NaCl	" $= -64$	
	" " acetic acid added	" $= -71$	
	" " hydrochloric acid added until precipitate formed redissolves	" $= -78.7$	

2. $[\alpha]_D = -62.6$ to $-64.6°$[4]

3. Serum albumin crystals.

Third crystallization	$p = 2.07$	$[\alpha]_D = -62.6°$	[5]
Still further purified	$p = 2.345$	" $= -60.1$	

4. Serum albumin crystals

Water	$p = 3.92$,	$[\alpha]_D = -61.2°$	[6]
"	$p = 3.2$	" $= -61$	
Third crystallization:		" $= -64$	

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[1] Framm *Loc cit*

[2] de Bary Hoppe-Seyler's med.-chem Untersuch., 1, 71

[3] Hoppe-Seyler Ztschr für Chem. u Pharm v Erlenmeyer, 1864, p 737

[4] Starke Jahresbericht für Thierchemie, 1881, p 18

[5] Sebalien Ztschr. physiol Chem., 9, 439

[6] Michel: Verh d physik.-med Ges. zu Würzburg, 29, No 3

LACTALBUMIN.

Water, $p = 2\ 20$, $[\alpha]_D = -36.6°$ [1]
" $p = 3\ 32$, " $= -36.4$
" $p = 4\ 23$, " $= -37.0$
Another preparation " $p = 3.12$, " $= -38\ 0$

EGG ALBUMIN

1. Aqueous solution

Independent of the concentration.. .. .. $[\alpha]_D = -35\ 5°$ [2]
By addition of hydrochloric acid. . . . . " $= -37\ 7$

2 Dilute hydrochloric acid

$[\alpha]_D = -37.8°$ [3]

3. White of egg, fractionated by its solubility in ammonium sulphate solutions, gave

Fraction 1 soluble in concentrated salt solution, 3 75 per cent albumin . .. . $[\alpha]_D = -42.90°$ [4]
Fraction 2 soluble in half-saturated salt solution, 8 59 per cent albumin . . .. " $= -34\ 30$
Fraction 3 soluble in dilute salt solution, 6.48 per cent albumin.. .. . . " $= -25\ 13$

4. Ash-free egg albumin, wheat albumin and pea albumin made by the process of Harnack[5] The specific rotations refer to $[\alpha]_D$ [6]

			In acid solution		In alkaline solution		
					The acid solution treated with NaOH		
Ash-free albumin from	Prep	In 100 cc solution Gram	Not dialyzed	Dialyzed to turbidity and then cleared with HCl	until it became clear	to alkaline reaction with phenolphthalein	and further addition of 5 cc conc NaCl solution
Eggs ..	A	0 1365	....	−54 6°	−69 9°	−77 5°	−97 6°
	B	0 326	−57 0°		..	. .	..
	"	0 265	. .	−46 2	−66 8	−52 5	− 55 9
Wheat	A	0 287	.. .	−88 7	−99 3	.	....
	B	0.188	−93 0		..	.	...
	"	0 102	.	−72 6	..	−54 6	−31.0
Peas.		0 534		−83 7	...	−62 0	−60 2

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[1] Sebalien, Ztschr physiol Chem, **9**, 457, 459
[2] Hoppe-Seyler Ztschr für Chem u Pharm, 1864, p. 737
[3] Starke Jahresber f Thierchemie, 1881, p 18
[4] Bondzynski and Zoja Ztschr physiol Chem, **19**, 11.
[5] Ber d chem Ges, **22**, 3046, **23**, 3745, **25**, 204
[6] Bulow Pfluger's Arch f d ges Physiol, **58**, 219.

ALBUMOSES (Propeptones)[1]

Protoalbumose

Prep	Dissolved in hydrochloric acid of 0.04 to 0.08 per cent		Dissolved in sodium carbonate solution of 0.12 per cent		
A	$c^* = 1.588$	$[\alpha]_D = -72.6°$	$c^* = 2.198$	$t = 20°$	$[\alpha]_D = -81.2°$
B	" $= 2.277$	" $= -79.1$	" $= 2.223$	$t = 21$	" $= -70.6$
C	" $= 1.925$	" $= -77.9$	" $= 1.873$	$t = 23.5$	" $= -80.1$
"	....	....	" $= 2.361$	$t = 22.5$	" $= -79.2$
D	" $= 1.366$	" $= -73.2$	....	....	....
E	" $= 1.681$	" $= -71.4$	" $= 1.904$	$t = 24.5$	" $= -76.3$
"	....	....	" $= 2.494$	$t = 24.5$	" $= -75.3$

Deuteroalbumose

Hydrochloric acid with 0.06 p. c. HCl		$c^* = 1.680$	$[\alpha]_D = -74.4°$	
" 0.04 " "		" $= 1.517$	" $= -79.1$	
Soda sol. " 0.12 " Na_2CO_3	Prep *A*	" $= 2.537$	" $= -74.3$	(77.6)
" " " 0.12 " "	" *B*	" $= 1.765$	" $= -75.3$	
Salt " " 0.5 " NaCl	" *A*	" $= 1.287$	" $= -77.7$	(77.0)
" " " 0.5 " "	" *B*	" $= 1.916$	" $= -72.0$	

Heteroalbumose

Hydrochloric acid of 0.07 p. c. HCl....... $c = 1.748$ $[\alpha]_D = -68.65°$
Soda solution.............................. $c = 1.584$ " $= -60.6$

FIBRINOGEN.

1. Dissolved in 2 to 3 per cent. NaCl solution

		NaCl + ash		
From ox blood...........	$c = 0.426$	1.362 p. c.	$[\alpha]_D = -35.2°$	[2]
	$c = 0.414$	1.752 "	" $= -36.2$	
	$c = 0.318$	1.415 "	" $= -36.5$	
	$c = 0.263$	1.819 "	" $= -37.7$	
		Mean	" $= -36.8$	
From horse blood.........	$c = 0.808$	3.744 p. c.	" $= -50.5$	

Solutions with more than 0.5 per cent. of fibrinogen can not be polarized on account of the marked opalescence.

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*c ash-free

[1] Kühne and Chittenden Z. f. Biologie von Kühne u. Voit, 20, (n. F. 2), 25 to 48

[2] Cramer Ztschr physiol Chem., 23, 83

2. Dissolved in NaCl solution :

		NaCl + ash	
From horse blood........	$c = 0.205$	1.045 p. c.	$[\alpha]_D = -50.6$
	$c = 0\ 289$	1.141 "	" $= -51.5$
	$c = 0\ 532$	2.251 "	" $= -53.9$
	$c = 0\ 291$	2.409 "	" $= -54.1$
		Mean	" $= -52\ 5$

3 Dissolved in 0 1 per cent. solution of sodium carbona

	Na_2CO_3 + ash.	
$c = 0.481$	1.788 p c.	$[\alpha]_D = -46.7°$ [2]
$c = 0.225$	1.341 "	" $= -44.5$
$c = 0\ 400$	1.611 "	" $= -45\ 7$
$c = 0.592$	2.284 "	" $= -45\ 1$

SERUMGLOBULIN.

Salt solution... .... $[\alpha]_D = -47\ 8°$ [3]

CRYSTALLIN.

From the crystalline lens .

α-Crystallin	Water, $p = 3.29$,	$[\alpha]_D = -46\ 9°$ [4]
β-Crystallin	" $p = 3.12$	" $= -43.3$
"	" $p = 1.80$	" $= -43.1$

Albumoid from the crystalline lens

Water..............	$p = 2\ 33$,	$[\alpha]_D = -50\ 9°$ [5]
"	$p = 2\ 51$,	" $= -52\ 2$

VITELLIN.

$[\alpha]_D = -43\ 6°$ [6]
" $= -43\ 35$

SYNTONIN

From the myosin of muscles by solution in very dilu hydrochloric acid, or by action of strong hydrochloric acid (albumin Solution in very dilute hydrochloric acid

$[\alpha]_D = -72°$ (Independent of the concentration)

Almost the same rotation is found in weak alkaline solutio

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[1] Mittelbach Ztschr physiol Chem , **19**, 289
[2] Cramer *Ibid*, **23**, 86.
[3] Frédericq · Arch de Biolog , **1**, 17
[4] Morner Ztschr physiol Chem , **18**, 91, 99
[5] Mörner *Ibid* , **18**, 77, 88
[6] Chittenden and Mendel Jahresber f Thierchemie von Maly, 1895, pp 29, 33

On heating the hydrochloric acid solution in a closed vessel about 100°, the rotation is increased to

$$[\alpha]_D = -84.8°$$ [1]

ALBUMINATES

Formed by the action of strong potassium hydroxide solut on albumins. As maxima there were found

Albuminate from serum albumin................	$[\alpha]_D = -86°$
" " uncoagulated egg albumin....	" $= -47$
" " coagulated " "	" $= -58$
" " casein (solution in strong KOH Rotation variable with amount of alkali)... .	" $= -91$

CASEIN.

In magnesium sulphate solution..	$[\alpha]_D = -80°$
In water containing 4 cc of fuming hydrochloric acid, per liter	" $= -87$
In the smallest possible amount of sodium hydroxide solution	" $= -76$
In aqueous solution, as strong as possible........ ...	$[\alpha]_j = -117$

HEMIELASTIN

Water . . . . $p = 2.509$, $[\alpha]_D = -92.7°$ (approx.) [5]

Elastinpeptone.

Water ... . $p = 6.14$, $[\alpha]_D = -87.9°$ [6]

[1] Hoppe-Seyler Ztsch f Chem u Pharm von Erlenmeyer 1864, p 742

[2] Hoppe Seyler *Ibid*, 1864, p 757

[3] Hoppe-Seyler *Loc cit*

[4] Béchamp Bull soc chim, [3], 11, 152

[5] Horbaczewski Ztschr physiol Chem, 6, 337, 343

[6] Horbaczewski *Loc cit*

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ERRATA

On page 60, half the structural formula for xylose and xylonic acid is missing

On page 684, read *cinchonifine* for cinchonidine